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ATTENTION TO FISH AND BIOASSAY PROCEDURES FOR ASSESSMENT
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**ASSOCIATE COMMITTEE
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PULP AND PAPER WASTES,
WITH PARTICULAR ATTENTION
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**BY
J.R. MARIER**

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ENVIRONMENTAL QUALITY

**"THE EFFECTS OF PULP AND PAPER WASTES ON AQUATIC LIFE
WITH PARTICULAR ATTENTION TO FISH AND BIOASSAY PROCEDURES
FOR ASSESSMENT OF HARMFUL EFFECTS."**

by

J.R. MARIER

**Environmental Secretariat
Division of Biological Sciences
National Research Council of Canada
Ottawa, Ontario, Canada**

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The Associate Committee on Scientific Criteria for Environmental Quality was established by the National Research Council of Canada in response to a Federal Government mandate to develop scientific guidelines for defining the quality of the environment. The Associate Committee's program includes the quantitative assessment of risks to receptors from pollutants in the Canadian environment, together with the related fundamental principles and scientific knowledge. Members of the Associate Committee, its Subcommittees and Expert Panels, serve voluntarily and are selected for their individual competence and relevant experience with due consideration for a balance among all sectors in Canada.

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Comments on Associate Committee documents are welcome and will be carefully reviewed by the Expert Panels. It is foreseen that these scientific criteria may be revised from time to time, as new knowledge becomes available.

SUMMARY

The pulp and paper topic is of foremost importance to Canada and was selected as the first priority of the Subcommittee on Water of the NRC Associate Committee on Scientific Criteria for Environmental Quality. The concern of the Subcommittee was influenced by the fact that water usage in pulp and paper production is enormous: in 1966, it utilized 560 billion gallons per year and this is expected to rise to 720 billion gallons by 1980 and 1020 billion gallons by the year 2000. Although considerable information has been published on pulp and paper wastes, it is highly dispersed in the technical literature and needed to be assessed and presented in an integrated manner.

The report contains five major segments:

1. How characteristics of various types of water can influence the impact of various pollutants;
2. How wastes are produced by the various mill processes;
3. What substances are present in pulp mill wastes;
4. Adverse environmental effects of pulp mill wastes;
5. The various tests which can be performed to assess undesirable effects on aquatic ecosystems.

The report is aimed particularly at highlighting data which showed a gradation of effects caused by varying amounts of any pollutant and by different lengths of exposure to these substances. Special emphasis is placed on conditions that exist in nature itself, although references to laboratory studies are also included. It is important that we address ourselves to cause-vs-effect type of information if we are ever to develop a sound scientific basis for the protection of our environment which is ultimately man's vital life-support system.

What are some of the problems discussed in the report? One of these is dissolved oxygen. Just as human beings are dependent on the oxygen present in the air they breathe, so fish and other aquatic life are dependent on the dissolved oxygen content of the water. Pulp and paper wastes require oxygen for decomposition; the higher the amount of such wastes, the greater will be the demand for oxygen from the receiving waters. As the amount of waste becomes very large, the stress imposed on all aquatic organisms will be very serious. Another type of burden can be imposed by discharging wastes which are either very alkaline or very acidic and this "pH" factor is also discussed in the report. Yet another type of problem is created when large volumes of wastes containing appreciable quantities of suspended wood fibre are discharged; the fibres can eventually "blanket" the bottom of a waterway and this will result in suffocation of bottom-dwelling life and conditions may favor the formation of hydrogen sulphide; in addition, the possibility of detrimental slime growth will be greatly increased. Pulp and paper wastes can also contain several substances that are directly poisonous to sensitive aquatic organisms; the report presents data bearing on this toxic aspect of the problem. The dark coloring in some pulp and paper wastes reduces the penetration of sunlight into water and this in turn can have a bad effect on photosynthetic processes which need sunlight.

All of the above factors can act simultaneously to adversely affect an aquatic ecosystem. Therefore, the consideration of each factor separately can often be inadequate. For this reason, many researchers are convinced that the sum-total impact of pulp and paper wastes can best be evaluated by recourse to a laboratory test in which a responsive aquatic organism is exposed to the actual wastes. The report discusses features of such "bioassay" tests and points out that the conditions in these tests

are often not as severe as those in the actual outdoor environment. The report emphasizes that the "ecological health status" of the receiving waters is the important factor, rather than mere reliance on the composition of wastes in the outfall pipes.

Recommendations concerning various water quality factors are given at the end of the report. However, if there is one overall need, it is the establishment of a coordinated water quality "monitoring grid" covering all of Canada's major waterways. This would permit on-going assessment of their ecological health status, not only as affected by pulp and paper wastes, but also by all other forms of discharge.

FOREWORD

This monograph was written by J.R. Marier of NRC's Environmental Secretariat, at the request of the Water Subcommittee of the National Research Council's Associate Committee on Scientific Criteria for Environmental Quality; also, at the request of the Environmental Protection Service and the Fisheries Service of Environment Canada, for the "Working Group on Effluent Toxicity Requirements". This report covers the scientific literature that came to the author's attention prior to February 20, 1973.

The NRC Water Subcommittee appointed an Advisory Panel to review this report. The panel members were:

Dr. C.C. Walden (Panel Chairman):
British Columbia Research Council, Vancouver.

Dr. M. Waldichuk: Pacific Environment Institute,
Environment Canada, West Vancouver.

Mr. H.D. Paavila: Canadian Pulp and Paper
Association, Montreal.

Dr. R.H. Cook: Environmental Protection Service,
Environment Canada, Halifax.

Dr. R.P. Côté: Environmental Protection Service,
Environment Canada, Halifax.

The manuscript was critically reviewed and approved for publication by the Water Subcommittee and the Associate Committee.

La version française de ce document sera disponible aussitôt que possible.

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Perhaps the best way to begin this presentation is by quoting excerpts from Sprague's trilogy on "Measurement of Pollutant Toxicity to Fish", i.e.,

"...the worker in pollution biology is actually very well supplied with individualized bibliographies in this field. There is no need for him to lack background information on effects of a given toxicant. The problem may often be the reverse: an oversupply of unassimilated information, difficult to evaluate... A continuing quandary is how much detailed data to publish. Most journals and most readers are already burdened by today's voluminous literature, and long intricate papers seem inappropriate... This is not an exhaustive review of the literature, but a selection of research highlights, and of those approaches which seem most profitable..."

In any discussion of pulp and paper wastes, there are crucial considerations for Canada: a 1971 report estimated that, in 1966, the water usage in pulp and paper production was 560 billion gallons per year (i.e., 560×10^9 gal.), and that this will increase to 720 and 1,020 billion gallons for the years 1980 and 2000, respectively (see Reference: Montreal Engineering Co. Ltd.). Combined with this is the realization that a moderate size pulp mill (presumably a chemical pulp mill without chemical recovery) can produce waste that, in terms of its Biochemical Oxygen Demand (BOD), is equivalent to a city of several million people (See: Katz, 1971). Also, in terms of general pollution, there is evidence that, in certain regions, the capacity of some of Canada's receiving waters is already severely strained. Graphic illustrations of this dilemma can be seen in the situation on the Ottawa River (See APPENDIX 1) and in the Maritimes (Row, 1972) where, in both cases, pulp mills were found to be significant contributors to the "pollution load". Similar concern had previously been expressed about the situation in British Columbia (Waldichuk, 1962 and 1966), although the situation may have improved during recent years.

APPENDIX 2 presents a simplified flow-diagram of pulp and paper processes. The reader should note that there are two major segments in the complete operation, i.e., pulping and bleaching. However, pulp mills sometimes produce unbleached pulp as an end-product. When bleaching is part of the overall operation, the bleaching process is an adjunct to whatever pulping process is being used at a particular mill. As such, environmental problems relating to bleaching (or chlorination, etc.) will be discussed in the general context of the several pulping processes dealt with in this report, especially as Servizi *et al* (1966) have emphasized that bleach effluents contain substances carried over from pulping operations.

Anyone who seeks detailed information on pulp and paper processes is advised to consult the references to Libby (1962) and to Macdonald (1969).

PULP AND PAPER WASTES

INTRINSIC WATER FACTORS

Before discussing the problem(s) posed by pulp and paper wastes *per se*, several water factors have to be considered, because they can influence the toxic potential to fish or to the general aquatic environment.

1. Dissolved Oxygen:

As can be seen from the graph (APPENDIX 3) taken from Doudoroff and Shumway (1970), a high level of dissolved oxygen is required to sustain the performance of various fish species. The trends depicted in the graph support the claim that salmonid fish require a dissolved oxygen level of 7 to 8 ppm "to carry out all their necessary activities" (Katz, 1971), and also lend credence to the conclusion that the "incipient limiting level" of dissolved oxygen for salmonids is 2 ppm (Alderdice and Brett, 1957), although, for long-term exposure, this level seems excessively low. Williams, *et al* (1953) advocate that, for salmonids, water should have a dissolved oxygen content of "no less than 4 ppm" and, to allow a safety margin to compensate for respiratory and circulatory effects, favor a limit of 5 ppm; this minimum level is also recommended in another report (see U.S. Interior, 1967). Van Horn *et al* (1949), in conducting toxicity studies of pulp mill effluents, discarded all data for which the dissolved oxygen level fell below 4 ppm (see also: Howard and Walden, 1965). In their reports, Doudoroff and Shumway (1967, 1970) reveal great reluctance to recommend definite levels for dissolved oxygen; in their 1970 report, they prefer to advocate various "levels of protection" (illustrated in APPENDIX 4 using only two of the many possible concentrations). In this connection Katz (1971) has emphasized that the saturation solubility of oxygen in water is 9.1 ppm at 20° C, and 7.5 ppm at 25° C. In their 1967 report, Doudoroff and Shumway had stated:

"...a minimum of 5 mg/L for warmwater fish habitats and 6 or 7 mg/L for coldwater fish habitats, which have been recommended and widely accepted for a long time, cannot be overthrown... Being intermediate between the highest (most restrictive) and lowest standards that can now be reasonably defended, they are still as sound and as justifiable as any others."

However, this is somewhat lower than the 7 to 8 ppm levels of DO that Katz (1971) stated are necessary for salmonids. Furthermore, Hicks and DeWitt (1971) have cautioned against the assumption that what is deemed "safe" for aquatic life at an oxygen concentration of 9 mg/L would be safe in a receiving water having a dissolved oxygen content of only 5 mg/L.

2. The type of receiving water:

Briefly, this segment can be summarized by the statement: A seacoast is not an inlet, is not an estuary, is not a river, is not a lake. As an illustration of this, Waldichuk (1966) has reported that the shutdown of a sulfite mill for one week restored the dissolved oxygen level from its low value of less than 1 mg/L to "nearly normal" (i.e., between 8 and 9 mg/L) in a comparatively shallow tidal basin of British Columbia. In contrast, Ahling (1971) has stated that a similar shutdown in Sweden required 1 1/2 years to restore the heretofore-depleted oxygen saturation to more than 50% in the hypolimnion of a deep oligotrophic lake. Rosenberg (1972) reported that, after the closure of a sulfite mill, populations of benthic species in a Swedish lake required about 4 years to reach an apparent natural maximum in the sampling region closest to the source of pollution. These examples of oxygen depletion and/or renewal illustrate the crucial importance of considering the physical characteristics of the receiving waters (i.e., whether shallow or deep; stratified or mixed; laminar or turbulent flow, etc.). In the reports cited, Waldichuk (consult references) has striven to emphasize the distinctions and/or allowances that must be made with respect to the type of body of water involved in a waste-disposal program.

3. The pH of the water:

An overall appreciation of this aspect of the situation is provided in APPENDIX 5. This has particular relevance to pulp and paper effluents, because Waldichuk (1962) and Howard and Walden (1965) have shown that the pH of the various individual effluent-streams originating from the full-bleach kraft process can vary from less than 2 to over 12; moreover, effluent streams from the sulfite process generally range between pH 1.2 to 2.7 (Eloranta, 1970; Gunter and McKee, 1960; Nemerow, 1971). Katz (1971) has stated that the alkalies in kraft pulping wastes may increase the pH of rivers or lakes to a level too high for fish survival; however, extreme pH levels might also be expected from acidic wastes from sulfite pulping and acid-bleach sewers (Howard and Walden, 1965). It is relevant to point out that Waldichuk (1962) has discussed the role of seawater salts in contributing to the buffering capacity of marine waters receiving pulp mill wastes. In APPENDIX 5, the pH optimum of between 5 and 9 advocated in the EIFAC (1969) criteria is in accordance with the recommendations of Doudoroff and Katz (1950) and Katz (1971). However, Ladd was reported by Hicks and DeWitt (1971) to have found the limit pH (based on short-term TLM) for coho salmon to be at pH 3.9 and 10.1, whereas a report of a field study (U.S. Interior, 1967) recommends that the pH should be greater than 6.5 to protect fry and fingerling salmon. The pH range recommended in the EIFAC (1969) report is for long-term considerations.

4. Water temperature:

With lake trout, Gibson and Fry (1953) found an "upper lethal temperature" of 23.5° C, and a "temperature for maximum activity" of 15 to 17° C. Katz (1971) has stated that the "upper lethal limits" for salmonid fish species are between 23.7 and 25.9° C; for bass and catfish, the corresponding temperature is about 36.4° C.

5. Water hardness:

Grande (1964) has obtained evidence that indicates that the toxicity of pulp mill wastes may be greater than expected when released in extremely soft waters. Zinc is sometimes used in groundwood pulp bleaching, and it is pertinent to note that its toxicity to rainbow trout is about 4 times greater in soft water (total hardness: 20) than in hard (200) water (see reference to Brown, 1968; Inland Waters, 1972).

6. Other factors:

Such topics as suspended solids will be discussed in the subsequent sections specifically devoted to pulp and paper wastes.

PULP AND PAPER WASTES

ORIGIN OF PULP MILL WASTES

In Canada today, 4 pulping processes are in use: there are 50 groundwood installations, 39 utilizing the sulfite process (only 3 of which embody a recovery system), another 46 using the kraft (sulfate) process, and only 9 employing the semi-chemical "neutral sulfite" process (Neale, 1973). Thus, it can be seen that the bulk of the pulping operations involves 3 processes: groundwood, sulfite, or kraft. The same trend prevails in the United States (Amberg, 1970).

A brief description of each process seems appropriate:

1. Groundwood (or mechanical) pulping involves, as the name implies, a simple grinding (i.e., "defiberizing") of the wood. This non-chemical process produces a high lignin pulp with short fibres that is mainly used for newsprint after supplementing with kraft or sulfite pulp for added strength. Although the "waste production per ton of product" is regarded as relatively low, a considerable amount of small fibers can be released, and resinous wood constituents are leached during processing.
2. Sulfite processing normally involves chemical digestion in acidic bisulfite, and produces an easily-bleached high-quality cellulose fiber. During digestion, about 54% of the wood constituents are solubilized, leaving the cellulose fibers. Although 4 variants of this process can be used, what might be called the "traditional" calcium-base sulfite process does not usually have a recovery system because of corrosion, scaling, and other technical problems (Adams, 1968; Benjamin *et al*, 1969; Mueller and Walden, 1970; Perry and Woodland, 1970; Waldichuk, 1962; Whittle, 1971). Thus, disposal of spent sulfite liquor (SSL) can result in a very high Biochemical Oxygen Demand in the receiving stream, i.e., 500 to 1200 pounds of BOD per ton of pulp (Amberg, 1970). In reference to the sulfite process without chemical recovery, Waldichuk (1957) has stated that "in general, effluent from a given tonnage of sulfite pulp produces about 10 times as great a pollution hazard as that from an equal tonnage of kraft pulp." The data of Hedberg *et al* (1969) and Nemerow (1971, Table 24-13) indicate that, when compared to kraft wastes, sulfite effluent (without chemical recovery) can contain from 6 to 16 times more BOD per ton of pulp.

Alternative procedures for sulfite pulping are available, in which either ammonia, sodium, or magnesium is used instead of calcium. These "soluble base" alternatives facilitate the attainment of higher pulping yields and also make chemical recovery possible, although a recovery system is not always included in such operations (Neale, 1973). Of the alternatives, the ammonia-base process is the cheapest in terms of initial investment (Faulkender *et al*, 1970) and allows recovery of sulfur compounds but not usually of ammonia (Perry and Woodland, 1970; Whittle, 1971). However, Perry and Woodland (1970) have discussed a proposed "exchange recovery" method by which the ammonia could be recycled, but have also stated that the ammonia-base process produces a darker unbleached pulp. The sodium-base process has the most complex recovery system of the three processes (Perry and Woodland, 1970; Whittle, 1971); in contrast, the magnesium-base process has the simplest recovery system of the three alternatives (Keef, 1971; Perry and Woodland, 1970; Whittle, 1971). Recent reports (Adams, 1968; Mueller and Walden, 1970) have raised the question that the cost of operating recovery systems with these processes (ammonium, sodium, or magnesium) will be 4 to 5 times greater, per ton of pulp, than the calcium-base without recovery. However, Keef (1971) reported on a mill that had converted from calcium-base to recovery processes using ammonium, then sodium,

and finally magnesium-base pulping, in successive attempts to solve environmental problems; Keef's overall conclusion was that "a magnesium bisulfite system with chemical recovery represented the lowest operating cost and capital investment of the various proven pulping processes... while the BOD level has been reduced by more than 80%". Also, Pearson (1972) reported that a soluble-base sulfite mill in Scotland (with chemical recovery) produced effluents in which both the BOD and suspended fiber content of the effluent are "considerably lower than those of either the calcium-based sulfite process or the kraft process"; however, the comparison with the kraft process awaits further documentation.

3. Kraft (or sulfate) pulping involves digestion of the wood in an alkaline mixture of sodium salts (of which the predominant forms are sulfide and hydroxide) producing a very strong fiber that, although more difficult to bleach than sulfite fiber, is well suited for a variety of products in which strength is a desirable characteristic. In the process of digestion, about 52% of the wood is solubilized; but, unlike the conventional sulfite process, the kraft process includes a recovery system. Because of the added economics attained by recovery, and because the kraft process can duplicate the performance of the sulfite system with less water pollution hazard, kraft mills have been replacing sulfite mills in Canada during recent years. However, it is pertinent to note that many existing kraft process mills have air pollution problems, although these may be amenable to future abatement. Adams (1968) has reviewed the air pollution aspects of pulp and paper operations, and has emphasized that a major source of kraft mill odor arises because the recovery furnace is operated beyond design capacity. Studies are currently being conducted to develop a sulfide-free alkaline pulping process (CPAR, 1972; Worster and Pudek, 1972).
4. The neutral sulfite semi-chemical (NSSC) process involves partial delignification by chemical digestion in a mixture of sodium carbonate and sodium sulfite, requiring a short digestion time. This operation is generally considered to be a "high-yield" process, i.e., utilizing as much as 80% of the wood (Benjamin *et al*, 1969) and is thus regarded as having a relatively low water pollution potential, even though it rarely incorporates a chemical recovery system.

As stated previously, APPENDIX 2 presents a simplified flowsheet that illustrates the various steps involved in pulping processes. Anyone interested in more specific details can find such information in the references to Libby (1962) and Macdonald (1969). For environmental relevance, the report by Nemerow (1971) might be of special interest, because it includes a bibliography of 608 references.

PULP AND PAPER WASTES

SUBSTANCES PRESENT IN PULP MILL WASTES

Wood preparation:

Concern has often been expressed about the loss of bark, knots, pitch, sawdust, and small fibers in the untreated effluents (e.g., Eloranta, 1970; Smith *et al*, 1965; Systems Research Group, 1970; Waldichuk, 1970; Werner, 1963; Wilber, 1969). However, degradation products can also be present, because Havrankova and Tichy (1968) have demonstrated that wood-destroying fungi decompose cellulose and liberate lignin monomers of a phenolic character. Treatments of stored-wood piles with the fungicide sodium pentachlorophenate (Holland *et al*, 1960) may also introduce into the effluent a highly toxic chemical which remains active up to 2 months after its application, and has been found 4 miles downstream from the area of application (Côté, 1972-a). [Note: In Canada, use of pentachlorophenate in pulp and paper operations does not seem to have been widespread, and recent indications are that any use is being phased out; however, use of pentachlorophenate has recently been reported in other countries (Norup, 1972; Rudling, 1970) and reference will therefore be made to this topic in this report]. Hydraulic debarking results in losses into the water of sawdust, fibers, fines, bark and dirt (Neale, 1955). Cook and Hoos (1971) have reported that untreated debarker effluent can contain as much as 180 ppm "resin acids", making it "highly toxic". (Note: The reported values for "resin acids" were analyzed by Carpenter's 1965 method. This topic will be discussed later in this report).

Groundwood:

This process can result in a particulate effluent of screening rejects, wood fibers and cellulose fines (Neale, 1955). Row and Cook (1971) have found that groundwood effluents can contain approximately 50 ppm of "resin acids", about one-half of which is apparently associated with bark. Such a finding is probably greatly influenced by the type of wood being processed, because Waldichuk (1964) has pointed out that coniferous wood species contain the highest amounts of resin acids. Zinc hydrosulfite is sometimes used for bleaching ("brightening") of groundwood pulp, and significant concentrations of zinc have been found in the effluent (Munro *et al*, 1972).

Sulfite digestion process:

The effluents from the calcium-base process contain sulfur compounds, sugars, lignin residues, alcohols, acetone, volatile acids, and furfural (Nemerow, 1971). The major sulfur compound is probably bisulfite, although it has been reported as "sulfur dioxide" (Williams *et al*, 1953; Nemerow, 1971). The sugars comprise arabinose, fructose, galactose, glucose, mannose, and xylose (Maloney and Robinson, 1961), and the bulk of the lignin is in the form of lignosulfonic acid (Eloranta, 1970; Nemerow, 1971). The acids comprise acetic and formic acids (Eloranta, 1970; Faulkender *et al*, 1970). Chlorinated lignin and catechol have also been identified in the chlorination bleach effluents of sulfite mills (Collins *et al*, 1971; Eloranta, 1970). As stated previously, this effluent is acidic.

Kraft (Sulfate) process:

These effluents contain sulfides, mercaptans, lignin derivatives, resin acids and fatty acids or their salts (Alderdice and Brett, 1957; Haydu *et al*, 1952; Howard and Walden, 1965; Leach and Thakore, 1973; Rogers, 1973; Seppovaara and Hynninen, 1970; Van Horn *et al*, 1949; Werner, 1963). Other investigators have identified terpenes (Hynninen, 1971) which Nilsson and Rennerfelt (1971) consider as originating mostly from resinous woods such as pine. Waldichuk (1964) has pointed out that coniferous wood species such as pine contain the highest amounts of resin acids, and these are the wood species that engender major foaming problems in pulping or bleaching operations. Bruynesteyn

et al (1972) have shown that foaming concentrates the surface-active resin acids by approximately 5-fold; this suggests a means of removing resin acids by foam fractionation. The sulfide compounds can comprise an entire series (e.g., hydrogen sulfide, dimethyl sulfide, disodium sulfide) as well as other sulfur compounds such as methyl mercaptan; however, Hynninen (1971) and Werner (1963) have concluded that hydrogen sulfide only occurs in digester solution (i.e., "Black Liquor"), whereas methyl mercaptan is the predominant component of the condensate(s). Chlorinated lignin has been found in the acidic chlorination bleaching effluent of kraft mills (Kempf and Dence, 1970; Waldichuk, 1970). Das *et al* (1969) have identified tetrachloro-o-benzoquinone, and other authors (Rogers, 1973; Servizi *et al*, 1966) have discussed the presence of polychlorinated forms of guaicol and catechol in kraft bleach wastes.

Overall:

APPENDIX 6 lists the various components identified in various pulp and paper effluents. These lists may not be complete, but they do give an indication of the complexity of the effluents that are produced. And, to further complicate matters, various substances can be added, e.g., chlorine or zinc hydrosulfite as "bleaching" agents (Katz, 1971; Nemerow, 1971; Waldichuk, 1964 and 1970), mercurials (in the past) or the sometimes-used sodium pentachlorophenate as slimicides (Nemerow, 1971; Pearson, 1972; Systems Research Group, 1970; Wilber, 1969), and higher alcohols as anti-foam agents (Shumway and Chadwick, 1971). Thus, it can be appreciated that assessment of the pollution impact of pulp and paper effluents is a complex task. As an illustration of the dilemma, Conkey (1969) lists 334 biostatic compounds (fungal and bacterial growth inhibitors) which may be used by the pulp and paper industry.

PULP AND PAPER WASTES

ADVERSE EFFECTS OF PULP MILL WASTES

In an attempt to avoid chaos or confusion, this general topic will be treated in 4 segments, i.e., suspended solids, oxygen demand, individual toxins, and "total impact" of wastes. This will sometimes involve reference to bioassay tests; however, the intention is to deal with bioassays *per se* in a subsequent section of this report.

a) Suspended Solids:

APPENDIX 7 presents "tentative criteria" proposed for suspended solids in receiving waters, concerning "the maintenance of freshwater fisheries". It can be seen that, for optimum protection, suspended solids concentrations less than 25 ppm are recommended. In this connection, Betts and Wilson (1967) have stated: "Suspended solids in the effluent discharge must be very low, of the order of 36 ppm, but with the proviso that this standard might be lowered still further". Sprague and McLeese (1968-b) have stated that plugging of gills by particulate matter has been found to be one important reason for fish death (see also MacLeod and Smith, 1966; Pearson, 1972).

In a comparison of the lethality to fish of "suspended wood fibers", Smith *et al* (1965) concluded that groundwood pulps were more lethal than chemical pulps, and that conifer groundwood produced the most lethal fiber. This could be attributed to the greater resin acid content of the coniferous wood (Waldichuk, 1964) or to the fact that conifer fibers have a relatively long needle-like structure (Walden, 1972).

Suspended solids will also increase the turbidity of the receiving waters, and this can interfere with conditions that favor "good fish fauna" (EIFAC 1964, Fig. 1). In a lake or similar site, this can contribute to what Eloranta (1970) has termed a "lignotrophic" condition, in which the reduced penetration of sunlight affects the phytoplankton. Parker *et al* (1972) have reported that effluent from a kraft mill at Alberni Inlet, B.C. resulted in colored and turbid waters which caused a 33% per foot-depth average extinction of incident light. This resulted in most photosynthetic organisms being limited to the surface waters, which in turn caused much lower dissolved oxygen levels and increased bacterial concentrations in deeper waters. Lee, Mueller and Walden (1972) have been more specific, indicating that the kraft effluent absorbs light to a great extent in the 400 to 550 m μ range, which covers the blue (430 m μ) but not the red (662 m μ) absorption peaks of chlorophyll "a". Eloranta (1970) observed a case where sulfite mill effluents allowed only 7 to 8% of the incident light to penetrate to more than 1 meter of depth, with unfavorable effects on phytoplankton.

Waldichuk (1970) has stated (in connection with a reduction in light penetration):

"There is no doubt that this leads to a reduced photosynthesis. By virtue of the reduction of phytoplankton, the grazing by zooplankton becomes affected. Thus, in the long run, the food supply of salmon can be reduced by reduction of light penetration..."

Note: Katz (1971) has warned that fish, in all of its stages, may be more tolerant to pollutants than phytoplankton or zooplankton. However, the question of "which trophic level or what stage of development is most sensitive to pollutants" does not find a simple answer. For instance, Servizi *et al* (1966) have obtained data indicating that adult salmon may have a lower tolerance to kraft wastes than fingerlings, and they suggest that this may be due to the comparatively greater activity of the adult fish, with concomitant acceleration of metabolic rate and greater uptake of toxicants. On the other hand, Woelke (1967) recommends the use of embryo to assess the biological impact of pulp mill wastes on oysters.

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Suspended solids can also lead to benthal deposits (McKeown *et al*, 1968) which produce mats on the bottom of receiving waters, with resultant destruction of fish food and spawning grounds (Wilber, 1969).

(Note: The problem of *Sphaerotilus* slime is discussed later in the "Sulfite" segment of Section "d").

Pearson (1972) has stated that "the most serious effects of the establishment of such (benthic) conditions is the creating of an anaerobic blanket deposit of fiber and wood chips at the sediment surface which results in the complete elimination of the existing benthic fauna". Also, Waldichuk (1962) has reported that, as a result of such bottom sediments, crabs and other invertebrates are "wiped out"; moreover, the sediments generate H_2S and, when dredging operations stir up the bottom, a fish kill may occur. Such anaerobic production of H_2S has also been emphasized by Werner (1963), who considers that pollution by suspended particulates is a more serious matter than that caused by other components present in effluents. One concluding comment is warranted: In the evaluation of the effects of pollutants on aquatic ecology, particular attention should be paid to invertebrates and other bottom fauna because, to use the phrase written by Brown *et al* (1970), these organisms are "continuously and unavoidably exposed... and unable to escape from the polluted zone". Recent reports (Alabaster, 1972; Pearson, 1972) have emphasized that settleable solids can contribute to deoxygenation of water, with consequent elimination of oxygen-dependent species in the affected zone.

b) Oxygen Demand:

The Biochemical Oxygen Demand (BOD) in aquatic ecosystems can be increased by 5 phases of pulp and paper operations (Systems Research Group, 1970): (a) silt and organic matter contributed by erosion in logging practices; (b) bark, wood chips and sawdust from wood preparation; (c) wood fibers from processing; (d) sugars, tannins, lignins, phenolic compounds, or catechols extracted during pulping; (e) conversion of waste sulfite to sulfate, as a consequence of sulfite pulping. The present report has already alluded to the fact that sulfite wastes (without chemical recovery) cause a much higher BOD than those released from kraft pulping (Waldichuk, 1957; Hedberg *et al*, 1969; Nemerow, 1971). In contrast, wastes from groundwood operations are considered to have a low pollution (i.e., BOD) potential and some reasons for this are shown in APPENDIX 8. The relatively low "Total Soluble Solids" content of kraft waste (APPENDIX 8) is to be expected, because the kraft process embodies a chemical-recovery system. In comparison, conventionally pulped (and unrecovered) sulfite wastes contain between 6 and 16% solids; of these solids, sugars account for 17 to 22%, in addition to 9 to 17% sulfur (or its compounds), 4.5 to 5.5% calcium, and about 5% "resin plus fats"; however, 45 to 52% of the solid material is lignin (Eloranta, 1970; Nemerow, 1971). Gunter and McKee (1960) have stated that the rapidly-attained high BOD of sulfite waste liquor (SWL) is largely attributable to sugars, 90% of which are decomposed in 10 days, whereas Nemerow (1971) has reported that sugars account for 65% of the 5-day BOD.

Although BOD is usually expressed on a 5-day basis, Howard and Walden (1965) have stated that this "does not reflect the continuing demand that cellulosic fibers may place on a receiving body of water". Several workers have illustrated the long-term oxygen demand of chemically-polluted industrial wastewaters (Gates and Ghosh, 1971; Grady, 1971; Hennequin, 1970; Raabe, 1968; Razzell, 1972), and have advised against over-reliance on 5-day BOD as a means of assessing long-term demand in receiving waters. Raabe's data (1968) were obtained in a stream receiving kraft wastes, and a comparative study of decomposition constants led him to suggest that "lignin and its by-products"

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were involved in the slow long-term decomposition. Razzell (1972) has published very similar conclusions. Such observations recall the statement made by Gunter and McKee (1960), i.e., "that lignin is susceptible to ultimate biochemical decomposition is generally recognized", although almost none of the 5-day BOD is attributable to lignin. Several authors have recently recommended that more consideration be given to this long-term phase of BOD (Hofsten and Edberg, 1972; Pearson, 1972; Wilber, 1969). Raabe's findings are illustrated in APPENDIX 9, where it can be seen that the 100-day BOD was about 3 times greater than the 5-day BOD, even though only about 50% of the lignin compounds were oxidizable "under test conditions". In commenting on the plateau stage that intervenes between the fast and the slower stage(s) of BOD, Grady (1971) states that the beginning of the plateau coincides with "the low point of the dissolved oxygen sag curve".

Several authors have stated that volatile reduced bivalent sulfur compounds are readily air-stripped or oxidized in receiving waters (Alderdice and Brett, 1957; Haydu *et al*, 1952; Walden and Howard, 1971). Nemerow (1971) has reported that sulfur compounds from sulfite wastes impose an "immediate oxygen demand" which accounts for about 11% of the 5-day BOD. The situation appears to be reversed in kraft condensate, because Seppovaara and Hynninen (1970) have reported that 75% of the 5-day BOD could be attributed to hydrogen sulfide and mercaptans. A similar observation had been made by Howard and Walden (1965) who stated that: "With few exceptions, those individual (kraft condensate) streams with a high content of sulfides and mercaptans also have high (5-day) BOD values". Servizi and Gordon (1972) have observed that a high BOD of kraft effluents is associated with spills of digester solution (i.e., "Black Liquor"). As previously mentioned, black liquor contains hydrogen sulfide (Hynninen, 1971; Werner, 1963). However, it is pertinent to point out that Howard and Walden (1965) have reported that, in kraft operations, half of the total oxygen demand originates in the bleaching streams of the process. Perhaps of greatest significance to this report, Howard and Walden (1965 and 1971) have shown that the correlation between the 5-day BOD and toxicity-to-fish of several types of kraft mill effluent is poor (see APPENDIX 10-a). As to methodological considerations, Razzell (1972) has urged the use of acclimated seed in the test, as a general precaution to avoid underestimation of BOD, although Walden *et al* (1972) have observed only minor differences when comparing acclimated and non-acclimated inoculum in BOD tests on bleached kraft effluent.

Chemical Oxygen Demand (COD) has also been used as a criterion, and may be a more realistic measurement of total oxygen demand. Whereas conventional BOD assays require 5 days, the COD provides a result within hours (Hennequin, 1970; Howard and Walden, 1971). On the topic of COD, Fujiya (1961) has recommended that the level in receiving waters should be kept below 10 to 50 mg/L to avoid damage to fish, and Wilber (1969) has stated that this type of research should receive more attention in all water pollution studies. Hennequin (1970) has cautioned that generalizations are not possible regarding a correlation between COD and BOD, and Walden *et al* (1971) have stated that COD can only be used as "a rough approximation" of BOD. A study by Davis (1971, Fig. 3) has indicated that the color of kraft effluent is in linear correlation with COD, but in curvilinear correlation with 5-day BOD; however there is no reason to expect that this would be a general occurrence.

Whereas a COD result can be obtained within a few hours, the Total Organic Carbon (TOC) test can be done within minutes (Howard and Walden, 1971), and has been termed "a very good approximation of total organic matter" (translated from Hennequin, 1970). Although Howard and Walden (1971) have demonstrated that there is no consistent correlation between TOC and COD (APPENDIX 10-b), Walden *et al* (1971) have stated that the correlation between TOC and COD "is quantitative

for many effluents", with COD being 3.5 times TOC. However, TOC does not even provide as good a correlation with toxicity as that obtained using 5-day BOD (Walden *et al*, 1971).

In general, it can be said that recent studies have shown that there is no consistent correlation between BOD (or either COD and TOC) and toxicity of pulp and paper wastes to fish. Nevertheless, such estimates of potential oxygen demand, especially when assessed in terms of the volumes of effluent released, provide a useful index of "loading rate" in receiving bodies of water. Such "loading rate" considerations are important not only with regards to long-term consequences, but also in assessing the short-term capacity of receiving waters to cope with the influx of wastes. Razzell (1972) has recently emphasized the need for comparative TOC, COD, and BOD data in the assessment of waste problems.

c) Toxicity of individual components:

APPENDIX 11 presents data on the toxicity of sulfur compounds that occur in kraft wastes; data for sodium hydroxide are also included. The trend is not meant to be interpreted as being strictly quantitative, but merely to illustrate that only very low levels of sulfide(s) and mercaptan can be tolerated by various fish species. However, recent reports indicate that embryonic and juvenile fish may be adversely affected by waterborne H_2S levels even lower than those listed in APPENDIX 11 (Adelman and Smith, 1970; Smith and Oseid, 1970).

Hynninen (1971) and Werner (1963) have shown that hydrogen sulfide in kraft effluents originates solely from the digester solution (i.e., Black Liquor), whereas methyl mercaptan is found in the cooking-plant blow-off condensates. Although the chemical-recovery feature of kraft processing is designed to minimize the release of these toxic compounds to the aquatic environment, such losses do occur (Betts *et al*, 1971; Bruynesteyn *et al*, 1972; Dhaneshwar *et al*, 1970; Servizi and Gordon, 1972). In a field study, Van Horn *et al* (1949) had shown that toxic levels of sulfides and mercaptan could be present in localized areas of receiving waters. Some researchers (Fujiya, 1961; Seppovaara and Hynninen, 1970) have described organic damage resulting from systemic poisoning of fish; moreover, in a study of kraft condensates, Seppovaara and Hynninen have concluded that: "... the *principal* source of the toxic disturbances was the definite sulfur compounds...". However, Walden and Howard (1971) have questioned such conclusions.

Where sodium hydroxide is concerned, the data in APPENDIX 11 indicates a different tolerance by the salmonid species used by Haydu *et al* (1952) compared to the spotfin shiners and minnows used by Van Horn *et al* (1949). This may be a pH effect, although the authors have not presented data on this aspect.

Another potential source of concern arises from the use of the ammonia-base sulfite process, in which ammonia is not recovered (Perry and Woodland, 1970; Whittle, 1971). The toxicity of ammonia is influenced by the temperature and pH of the receiving waters, as illustrated in APPENDIX 12.

The toxicity to fish of several substances is listed in APPENDIX 13. Once again, this Table is not meant to be definitive, but merely illustrates the toxicity potential. Several investigators (Betts and Wilson, 1967; Betts *et al*, 1971; Howard and Walden, 1965; Servizi *et al*, 1966) have suspected that the relatively high toxicity of bleach effluents might be due to chlorinated lignins. Work by Das *et al* (1969) has implicated tetra-chlorobenzoquinone as a toxic component of bleached kraft effluent. Kempf and Dence (1970) have shown that from 55 to 65% of the applied chlorine remains organically bound to lignin, of which one-third is found in effluent (Note: presumably, the remaining 2/3 is NaCl); also, they have found that lignin-bound chlorine is alkali-labile. Of relevance is the fact that Betts and

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Wilson (1967) reported that removal of free chlorine did not reduce the toxicity of bleach effluent. Betts *et al* (1971) Rogers (1973) and Servizi *et al* (1966) have stated that bleached alkaline effluent contained catechol-type compounds which, as Walden and Howard (1971) pointed out, are closely related to the toxic tetrachlorobenzoquinone identified by Das *et al* (1969). However, it does not seem possible to quantitate any toxic effect of chlorinated lignin (or related) compounds at this time.

As mentioned previously in this report, sodium pentachlorophenate has sometimes been used as a slimicide, and it has been found to accumulate in aquatic organisms (Côté, 1972-a; Holland *et al*, 1960; Norup, 1972; Rudling, 1970). Côté (1972-a) has reported that sodium pentachlorophenate is toxic to various aquatic organisms at concentrations ranging from 40 ppb to 2 ppm. Aside from its toxic potential, sodium pentachlorophenate may incorporate another undesirable feature, especially as Curtis *et al* (1972) have reported that it can impart a musty taint to food. This may be a general property of chlorinated phenols which have been said to impart a taste to fish and oysters at water-borne concentrations as low as 0.001 ppm (Katz, 1971). The fact that phenol concentrations as low as 0.001 ppm can impart an objectionable taste to water following marginal chlorination (see Standard Methods, 1960; EIFAC, 1972) illustrates that chlorination of phenols readily occurs in aqueous systems.

Here, it must be stated that while "taste" cannot be defined as a toxic property, the problem can seriously impair the economic health of fisheries and therefore deserves consideration. An undesirable smell in fish flesh is yet another problem, and Seppovaara and Hynninen (1970) have associated this with the use of pine which, in turn, Nilsson and Rennerfelt (1971) have associated with terpenes. Hynninen (1971) also attributes an undesirable odor to terpenes as well as to resin acids. These observations confirm earlier work done by Ebeling (1940).

The toxicity of resin acids has been known for a relatively long time (e.g., Van Horn *et al*, 1949; Alderdice and Brett, 1957; Waldichuk, 1964); however, it has only been within recent years that a great deal of interest has focused on this topic (Bruynesteyn *et al*, 1972; Cook and Hoos, 1971; Leach and Thakore, 1973; Rogers, 1973; Row and Cook, 1971; Walden and Howard, 1971; Worster and Pudek, 1972). These recent observations may have prompted Walden and Howard (1971) to state: "Thus, there is a tendency to implicate resin acids as being responsible for any toxicity problems in receiving waters." However, APPENDIX 14 illustrates that, on the basis of mixed "resin acids" content, considerable variability has been found in toxicity evaluations of various process streams. Some variables can be ruled out, e.g., all the investigators used salmonid fish for their bioassays; all resin acid determinations were made with the same procedure (see Carpenter, 1965). However, one discrepancy is difficult to explain: Curves 3 and 4 of APPENDIX 14 were both obtained from data by Row and Cook (1971) and both were studies of groundwood effluent, although from different mills. One of the reasons for the different trends between curves 3 and 4 may relate to the work of Munro *et al* (1972), who have shown that the use of zinc hydrosulfite for bleaching groundwood produces effluents that are about 3 times more toxic than if sodium hydrosulfite is used; moreover, the toxicity of zinc seems to be increased additively by the presence of organic compounds (i.e., high COD) in the effluent. However, this would not explain the difference between all 4 trends shown in APPENDIX 14.

The Carpenter (1965) method for "resin acids" is a non-specific colorimetric procedure that measures a mixture of acids of the abietic or pimaric types. The various resin acids differ in their individual toxic properties, and may occur in variable proportions among different wood species. The colorimetric method is therefore non-specific, and may produce artifactual results; nevertheless, it has been used for

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analysis of pulp mill effluents, and results have been presented herein on a composite "resin acids" basis (APPENDIX 14).

However, a more recent procedure is coming into use for analysis of resinous substances in pulp mill effluents, and is based on ion-exchange fractionation, followed by a combination of chromatography and mass spectrometry (Rogers *et al*, 1972; Leach and Thakore, 1973; Rogers, 1973). With this procedure, the predominant resin acid moieties in pulp mill effluents were found to be isopimarate, abietate, and dehydroabietate (Leach and Thakore, 1973; Rogers, 1973).

In a study of unbleached kraft pulping effluent, it was found (Leach and Thakore, 1973) that 55% of the toxicity was attributable to isopimarate, 22% to abietate, and 5% to dehydroabietate, whereas the remaining 18% of the toxicity was caused by a mixture of unsaturated fatty-acid soaps (i.e., linoleate, oleate, linolenate, and palmitoleate). However, Rogers (1973) has reported that resin acids are also present in bleach effluents, and has tentatively identified trichloroveratrole, which he believes to be derived from trichloroguaicol or trichlorocatechol originally formed by reaction of phenolic lignin residues in the chlorination bleach process. Leach and Thakore (1973) have commented that wide inter-mill variation in effluent toxicity might be related to different concentrations of wood extractives in the various wood species used for pulping. Therefore, the "wood species" factor may account for some of the difference in the trends shown in APPENDIX 14. But, whatever the individual factors are that contribute to toxicity, APPENDIX 14 illustrates that the use of log:log plots produces linear relationships for toxicity of pulp and paper effluents.

Several researchers (Betts and Wilson, 1967; Howard and Walden, 1965; Seppovaara and Hynninen, 1970) have obtained results that strongly suggest that antagonisms, synergisms, and/or potentiations influence the net toxicity that a given effluent may possess. Furthermore, it is difficult to argue with the logic of Walden and Howard (1971): "...the inherent toxicity of pulping effluents is ill-defined and the proportion of toxicity, attributable to known and unknown molecular constituents, has not been quantitatively assessed. Even this amount of information is lacking for the bleach plant effluents"; thus, the conclusion by Howard and Walden (1971): "The toxicity of..... effluents can only be monitored by direct assay."

d) "Total Impact" toxicity of pulp and paper effluents:

In this section, an attempt will be made to discuss the total impact of various pulp and paper effluents, and also to consider some of the interrelated factors that may aggravate or alleviate the toxic effect(s).

d-i) Wood preparation and Groundwood:

Untreated debarker effluent was found to be highly toxic to Atlantic salmon parr, and could contain as much as 180 ppm of "resin acids" (Cook and Hoos, 1971). Groundwood effluents were found to contain "resin acids" concentrations in the order of 50 ppm (Row and Cook, 1971). To interpret this in terms of receiving waters, some idea of the dilution factor is needed: Haydu *et al* (1952) have used a dilution factor of 1:20 in "simulated stream" studies, and Waldichuk (1962) has reported "an immediate dilution" of 1:20 in actual field studies. In contrast, Van Horn *et al* (1949) have reported that the lowest dilution observed in 2 streams was 1:73. A glance at APPENDIX 14 conveys the impression that, in spite of the various trends shown, concentrations of 50 to 180 ppm resin acids may be in the "4-day toxic" range if the dilution factor is in the range between 1:20 and 1:73 in the immediately-adjacent receiving streams. Also, Munro *et al* (1972) have shown that bleaching of

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groundwood pulp with zinc hydrosulfite will increase the toxicity of groundwood effluents, particularly when these have a high COD.

d-ii) Sulfite:

The concentration of "Sulfite Waste Liquor" (SWL) in effluents or receiving streams has traditionally been estimated by a variation of the Pearl-Benson test (see Barnes *et al*, 1963), and the assay depends on the conversion of lignin sulfonates to colored nitroso compounds. As such, the method is related to the solids content of SWL, which (in the digester) usually comprises about 10% solids (Wilber, 1969).

APPENDIX 15 presents a composite tabulation of some of the effects that have been reported following exposure of various aquatic species to SWL. These data are presented to illustrate the relative susceptibility of various aquatic organisms to SWL. Additional data on this topic can be obtained by reference to other reports (e.g., Holland *et al*, 1960; Neale, 1955; U.S. Interior, 1967).

In his field study, Grande (1964) reported a riverborne SWL concentration averaging between 50 and 100 ppm, with a maximum of 500 ppm. If we assume that the SWL leaving the digester has a concentration of 10%, but that post-digestion process dilutions reduce this to 0.3% SWL at the outfall (Paavila, 1972), then Grande's range of 50 to 100 ppm SWL indicates a stream dilution of 1:60 to 1:30. This is comparable to the dilution range observed in other field studies (Van Horn *et al*, 1949; Waldichuk, 1962) in the immediate proximity of the outfall.

In APPENDIX 15, the data on oysters are included for comparative purposes. Here it must be remembered that, unlike fish, oysters and other shellfish constitute a "captive audience" insofar as pollutants are concerned. Thus, long-term exposures are to be expected, in comparison to the transient exposures to which fish may be subjected.

Additional comments are relevant. Whereas Wilber (1969) reported that acidity of SWL did not contribute to toxicity in oysters (because the toxicity was unaffected by neutralization of the effluent), Grande (1964) demonstrated that the acidic waters (i.e., pH 5.39 to 5.49) in his field study might have increased the toxicity of sulfite effluents to trout. Moreover, Wilson (1972) has shown that SWL, at concentrations above 500 ppm (but particularly above 2000 ppm) can decrease the pH of a stream, i.e., from pH 6.5 to 4.5. However, in his own study, Grande (1964) was dealing with an innately acidic stream (pH 5.85) that, moreover, was a very soft water. Thus, here again, we are confronted with a situation wherein an effluent's effect on pH may depend on the buffering capacity of the receiving waters (Waldichuk, 1962), especially at relatively low concentrations of effluent. Wilson (1972) has demonstrated that SWL can also affect dissolved oxygen, i.e., lowering DO by approx. 1 mg/L for each increment of 1000 ppm SWL... this, in a water whose original DO was 8.5.

The topic of *Sphaerotilus*-induced slime growth merits discussion here, because it seems to have been reported mainly in connection with SWL. Neale (1955) has stated that SWL concentrations of 25 ppm or higher promote *Sphaerotilus* growth, while Holland *et al* (1960) consider that the extent of slime formation on fish eggs is directly proportional to the SWL concentration, and Alabaster (1972) has commented that *Sphaerotilus* growth on eggs is a factor in their mortality. Anderson and Beirwaltes (1971) have reported that the major SWL (i.e., SSL) components which promote *Sphaerotilus* growth include hexose sugars and acetic acid; they also report that *Sphaerotilus* organisms can grow at BOD levels as low as 0.06 ppm, and that aeration appears to be an important factor in reducing slime growth. Eloranta (1970) has pointed out that this type of slime can grow on submerged vegetation and

stones, and can thus create conditions even more unfavorable than those caused by wood fibers. It is relevant to point out that Servizi *et al* (1966) have reported on the toxic effects of slime, the quantity of which appeared proportional to the concentration of neutralized bleach waste from a kraft mill; however, they did not mention *Sphaerotilus* by name.

d-iii) Kraft effluents:

In contrast with the manner of reporting data on Sulfite Waste Liquor, the work on kraft effluents is usually given as the “% dilution” of the effluent that will produce an effect (e.g., 50% of the fish killed) in a given period of time; or, the work is presented in terms of the time(s) required to produce a specific effect. Thus, where the criterion is that 50% of the fish are killed, we find the terms LC₅₀ (Lethal Concentration, 50%) or TLM₉₆ (Tolerance Limit, median: 96 hours), MST (Mean Survival Time) or Incipient Lethal Concentration (consult Sprague, I-1969). Variations of these basic modes of expression are also encountered, and it is sometimes difficult to relate one investigator’s results to those of another.

Walden and Howard (1971) have presented an excellent summary of the effects of kraft mill effluents, and the reader is advised to consult this source for details that may not be included in the present report. As stated in a previous section, kraft effluents have a much lower water pollution potential than those from conventional sulfite pulping; nevertheless, Walden and Howard (1971) have emphasized that problems can arise “solely because of the tremendous volumes discharged.”

Howard and Walden (1965) and Waldichuk (1964) have each studied the characteristics of 10 individual kraft mill effluent streams. Although the kraft digestion is an alkaline process, the acid bleach effluent is very acidic (pH 1.9 to 2.6); moreover, the combined whole effluent from a full-bleach kraft operation is also acidic (pH 2.6 to 3.2). Toxicity studies of kraft “whole effluent” led Howard and Walden (1965) to conclude that 75% of the toxicity is attributable to low pH; also, they concluded that one-half of the oxygen demand originates in the bleaching process. However, Walden and Howard (1971) consider the caustic bleach-plant effluents more toxic than those originating from the pulping process or from the acidic bleach streams. In contrast, Betts and Wilson (1967) have reported that “the chlorination effluent was by far the most toxic” and further found that “by removing the free chlorine there was no apparent change in the toxicity of the effluent.”

Strictly as a broad illustration, APPENDIX 16 presents some toxicity interrelations for various kraft mill effluent streams. These data were compiled from the reports of various authors (Alderdice and Brett, 1957; Betts and Wilson, 1967; Bruynesteyn *et al*, 1972; Cook and Hoos, 1971; Sprague and McLeese, 1968-a). Also, it must be emphasized that all assays used various species of salmon: Alderdice and Brett used Sockeye; Bruynesteyn *et al* used Coho; the others used the Atlantic species.

Again, linear relationships were obtained with log:log plots (with the singular exception of one point *re* the “ALDERDICE” data). Another important feature is that, as expected, Black Liquor (digester effluent) was the most toxic stream, followed by evaporator condensate, then the other streams (including combined effluent). This priority, wherein black liquor is the most toxic, followed by condensate then by the other streams, is in accord with the observations of Howard and Walden (1965). **NOTE: A PREVIOUS SECTION HAS DISCUSSED THE POINT THAT, ALTHOUGH BLACK LIQUOR LOSSES SHOULD BE MINIMAL, THEY NEVERTHELESS OCCUR.** Yet another factor that appears in APPENDIX 16 resides in the slopes given by the data for “Combined, BETTS” and “Clarifier, COOK”: these slopes are in disaccord with those shown in the other trends;

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however, they approximate the slope for "Black Liquor". This poses the question of black liquor contamination, and such a contamination has been admitted by Betts *et al* (1971). Another thing to consider is that these are all fresh effluents (Note: during storage, the toxicity of such effluents decreases, as discussed later) and all of them would require a volume-to-volume dilution to 25% strength (or lower) to avoid killing 50% of the salmon in a 96-hour period (APPENDIX 16). Although there may be thresholds for these effluents (i.e., concentrations below which the fish are not killed during prolonged exposure), these are not evident in the trends depicted in APPENDIX 16. The topic of "no effect" thresholds is always a difficult one. For instance, although Howard and Walden (1965) did not observe fatalities in fingerling sockeye salmon after 4 days of a 21-day exposure to progressively increasing concentrations of neutralized kraft bleach effluent, Servizi *et al* (1966) reported fatalities in adults of the same species after 15 and up to 29 days of exposure to dilute concentrations of the same type of effluent.

Razzell (1972) has emphasized that both accidental spills and process variability can account for inter-mill differences in effluent composition. Servizi *et al* (1966) observed wide *intra*- mill variations in effluent toxicity, even when the mill was producing a constant grade of pulp. Such observations recall the "housekeeping" theme advocated by Waldichuk (1962):

"The objectives in prevention of pulp mill pollution are in no way incompatible with the principles of good housekeeping and economic operation of a mill. All materials which go down a sewer were purchased originally, and if economical recovery is possible, they constitute a gain for the pulp industry as well as for conservation of aquatic resources."

d-iv) Other factors that affect total "effluent impact":

There is evidence that storage of various effluents (especially with aeration) will reduce their toxicity to fish. For instance, an examination of the data by Howard and Walden (1965) reveals that static storage of neutralized bleach kraft mill effluent at 2° C caused a loss in toxicity of between 5 and 15% per day (average: 10% per day), whereas Sprague and McLeese's data (1968-b) indicates that storage of the same type of effluent at 15-21° C resulted in a loss of toxicity averaging 37% per day, although the toxicity was even less after bio-oxidation. Servizi *et al* (1966) have emphasized that bio-oxidation is effective in reducing toxicity of kraft bleach waste, whereas atmospheric oxidation is inadequate. The data of Wilson (1972) indicate that aeration of Sulfite Waste Liquor at 17° C only decreases toxicity by 3 to 8% per day, while Gunter and McKee (1960) have reported that the biodecomposition of SWL in receiving waters is about 12% per day. At the moment, it is impossible to quantify such limited data beyond the fragmentary estimates given above; however, it would seem that storage of effluents (preferably at higher temperatures) for several days will decrease their toxicity considerably. Unfortunately, there is no substantiative information on this aspect. Other factors that affect the toxicity of pulp and paper effluents will be discussed in the subsequent section(s) of this report.

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BIOASSAY

At the moment, bioassay is the only way (under controllable conditions) to assess the biological response of an aquatic organism to an effluent. An excellent trilogy of reports has been authored by Sprague (I: 1969; II: 1970; III: 1971), dealing with various considerations to be kept in mind when undertaking bioassay studies. APPENDIX 17 lists the topics covered in Sprague's reports. Corroborative information on bioassay techniques can be obtained from the reports by ASTM (1959), Betts *et al* (1967), Brown (1968), Brown *et al* (1970), Doudoroff *et al* (1951), Hunn *et al* (1968), Katz (1971), Sprague (1972), and Warner (1967). In the present report, it is not the intention to repeat everything that Sprague and other authors have said so well. Instead, attention will be focussed on a few considerations that seem especially relevant to this presentation.

APPENDIX 18 (parts i to vii) presents the methodological details (as many as could be found in the original reports) concerning the data that were depicted as linear relationships in APPENDIX 16. Note that in APPENDIX 18, the pH of the effluent was usually adjusted to neutrality. Thus, it is possible that the trends shown in APPENDIX 16 do not represent the full toxicity of those effluents that, normally, are either very acidic or alkaline. Katz (1971) has warned about the toxicity hazards of highly alkaline effluents, whereas Howard and Walden (1965) have shown that low pH can account for 75% of the toxicity in acidic effluent. The same type of consideration applies to dissolved oxygen (i.e., the "D.O." column in APPENDIX 18) which was often maintained at saturation. However, it is pertinent to state that, from an examination of the data of Alderdice and Brett (1957) and Hicks and DeWitt (1971), it is possible to estimate that a reduction of dissolved oxygen from 6.5 to 4.0 mg/L will approximately double or triple the toxicity of kraft mill effluent. Moreover, Hicks and DeWitt (1971) conclude that "It would be hazardous to assume that a kraft waste level deemed "safe" for aquatic life based on bioassays conducted at an oxygen concentration of 9 mg/L would be safe in a receiving water having a dissolved oxygen content of 5 mg/L."

This leads to the topic of "motivation" for the bioassay. When the bioassays are conducted to assess the toxicity of chemical components in pulp and paper effluents, it is reasonable to want to eliminate variables (such as excessive suspended solids, extreme pH, or low oxygen) thereby to obtain a measurement of the remaining intrinsic toxicity. However, when a bioassay is being done to assess the potential impact of a waste disposal problem, then it is essential that the assay should reflect the *in toto* toxicity of the effluents, including suspended solids. On this general topic, Wilson (1972) has stated: "... a bioassay procedure which attempted to ignore this aspect of the toxicity would be quite lacking in realism."

Another aspect of the data presented in APPENDIX 18 is that the criterion for toxicity is (usually) the time required to kill 50% of the fish. This criterion, from a strict toxicological viewpoint, is regarded as indicating the lethal threshold for the "average" fish. However, as Brown *et al* (1970) have emphasized, this type of parameter means that "a half, and not an insignificant fraction, of a (fish) population was killed", and they also emphasize that a criterion whereby even 10% of the fish are killed in 48 hours is unrealistically high in terms of the consequent long-term decimation of a fish population. Some people use application factors, although this is a political compromise. Brown *et al* (1970) consider that an application factor of 0.2-0.4 (re the 50% lethal conditions) is too high to be considered as a long-term safeguard, and Sprague (III: 1971) has supported this with the suggestion that the factor should be 0.1 or lower, which would seem to be especially relevant to long-term exposures. However, Howard and Walden (1971) have commented that, for complex effluents such as kraft streams, the use of application factors is not valid, and they have also stated:

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“Biologists have long recognized that knowledge of the lowest lethal concentration of a pollutant, as monitored by standard survival tests, cannot be considered to represent a safe concentration in terms of the survival and continued maintenance of natural fish stocks.”

Some years ago, Howard and Walden (1965) concluded: “The need has been stressed for a more sensitive biological assay with which to determine the maximum concentrations of kraft effluent which have no deleterious effect whatsoever upon fish.” This requires the use of some non-lethal parameter. A promising beginning has been made in the study of sublethal effects, notably by researchers in British Columbia. Servizi *et al* (1966) had reported “distress” in fish exposed to sublethal concentrations of kraft bleach waste; the symptoms included restlessness and cough-response. Schaumburg *et al* (1967) observed a significant increase in the rate of “coughing” in salmon exposed to kraft effluent concentrations lower than those which cause death in static bioassay. Walden *et al* (1970) studied ventilation rate and “cough response” in salmon and trout exposed to neutralized kraft pulping effluent or neutralized composite bleach effluent; the “minimum response concentration” for the 2 specific samples of effluent was 1.1% and 4.0%, respectively. This compares with an average EC_{50} value of 3.7% for the same type of effluent, as observed by Webb and Brett (1972) for growth-rate and food conversion efficiency in underyearling sockeye salmon. MacLeod and Smith (1966) had shown that minnows exposed to suspended conifer groundwood fibers exhibited reduced active metabolism and swimming endurance, but with increased hematocrit and gill-cleaning reflex. In this connection, Davis (1973) has emphasized that the use of filtered effluent samples allows estimation of “cough response” provoked by chemical solutes, but not of those induced by particulate substances. Doudoroff and Shumway (1970) have included consideration of such factors as swimming speed, growth rate, and hatching weight in the formulation of criteria for dissolved oxygen (see APPENDIX 3). McLeay (1972) has recorded the changes in blood composition in salmon, after “acute 12-hour” or “chronic 25-day” exposures to neutralized whitewater from kraft pulping; an overall summary of his observations is given in APPENDIX 19. Davis (1970) has listed various symptoms (or parameters) for assessment of sublethal effects, and these include ventilatory activity, cough response (especially concerning oxygen utilization), nervous depression, increased cardiac output, reduced arterial oxygen tension, altered hematocrit and/or blood pH, reduced swimming speed, and increased metabolic rate resulting from increased uptake of pollutants.

Walden and Howard (1971) have discussed the “acclimation” of fish to kraft effluents, and also, the “avoidance” reaction of fish to the same type of effluent. However, whereas acclimation can be induced and measured in captive fish held in bioassay tanks, one wonders if the avoidance reaction might not sometimes exert priority under certain conditions. Sprague (1966) has seen evidence that salmon can exhibit a strong avoidance reaction to pollutants such as zinc (i.e., a component of some pulp mill effluents), and Lloyd (1972) has mentioned that “It has long been recognized that a river may be fishless.... because the fish avoid the area”. Nevertheless, it would seem that there are conflicting opinions concerning avoidance reaction to pulp and paper wastes *per se*. Holland *et al* (1960) have observed that, although silver salmon (i.e. coho) exhibited an avoidance-reaction to sulfite wastes, it was insufficient to protect 95% of the fish; moreover, the same authors could not detect any avoidance of kraft wastes. In contrast, Sprague and Drury’s (1969) data led them to conclude that Atlantic salmon parr showed moderate avoidance to bleached kraft pulp mill effluent (i.e., BKME) concentrations of from 10 ppm to 10% (over which range only 3 of 60 test fish failed to show avoidance); lower concentrations were not avoided, but a lethal concentration of 56% was strongly avoided. Nevertheless, Sprague and Drury (1969) commented that “given no easy alternative of clean water, we could not depend on salmon to avoid almost lethal levels of BKME”. Davis (1973) reports

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that high sublethal doses of bleached kraft mill effluent (i.e., $>20\%$ LC_{50}) induce "loading stress" in the fish, as characterized by struggling and an overall restless behavior. In commenting on "adaptation", Davis (1973) suggests 2 possible reasons for this phenomenon: (i) the toxicity of the effluent decreases (as can occur in static bioassays); or (ii) the fish compensate for the sustained stress by adjusting their respiratory parameters. Davis (1973) also points out that respiratory distress occurs at progressively higher levels of dissolved oxygen as the concentration of kraft effluent is increased, an observation initially recorded by Alderdice and Brett (1957).

Species other than fish can be very vulnerable. For instance, McLeese (1970) has shown that lobsters do not avoid bleached kraft mill effluent concentrations as high as 20%. Furthermore, Sprague and McLeese (1968-b) have demonstrated that storage of bleached kraft mill effluent reduces its toxicity to salmon but not to lobster larvae, and they recommend that "...effectiveness of any waste treatment method should be tested against several species of aquatic organisms rather than one". Other authors have reinforced this idea. Parker *et al* (1972) have reported that, even though the "vitality of salmonid populations does not appear to have been depleted" by kraft mill effluent, there were rather large changes in plankton populations. (Note: In some instances, this could result in an apparent "avoidance" phenomenon). Another illustration of inter-species difference is offered by Côté (1972-b), who has observed that the toxicity of sodium pentachlorophenate varies much more between different types of molluscs than between fish species; in fact, some molluscs succumb to concentrations almost 4 times less than any of the fish species that he studied. With such considerations in mind, Woelke (1962, 1967 and 1968) has developed bioassay techniques using oyster embryos, which he recommends as a sensitive biological indicator.

Most of the research on the toxicity of pulp and paper wastes has been done with salmonid species, and this is understandable for the twin reasons of extreme susceptibility (to pollutants) of these species, and their economic importance. The temperatures used in bioassays are either those that are optimum for the fish, or those that prevail (on a seasonal basis) in the receiving waters; for a waste disposal assessment, perhaps the second choice may have more regional relevance.

Several researchers (Betts *et al*, 1971; Cook and Hoos, 1971; Howard and Walden, 1971; Servizi and Gordon, 1972; Waldichuk, 1970) have stated that some regulatory agencies require that pulp and paper effluents be diluted to a concentration of 65% (volume-to-volume) with unpolluted water prior to conducting bioassay tests. This concept has come to be regarded as "chiseled in stone", although the author of the present report has not yet found any scientific justification for the 65% dilution. However, some defense of this procedure can be made *via* the use of application factors. Walden (1972) has written that, assuming a 1:20 dilution of mill waste at outfall (= 5% effluent), and the TLM as being (for 96 hr.) 12 to 18 times the concentration at which the first signs of stress appear, one would expect 50% of the fish to survive for 96 hr in 90% effluent (i.e., $18 \times 5\%$); however, the concentration for 100% survival is roughly 70% of the TLM_{96} value (i.e., $90 \times 70\%$), or a 63% concentration of effluent. This does not agree with the data shown in APPENDIX 16. Moreover, Servizi *et al* (1966) have reported that a BOD reduction of about 60% (via biological treatment) is necessary to render neutralized kraft bleach waste "nearly non-toxic" to sockeye fingerlings in a 96-hr bioassay. And, although Brown *et al* (1970) have concluded, as a result of a field study, that "the median lethal concentration, for rainbow trout, of clean-water dilutions of the polluted fresh waters were found to be about 65% of those predicted from the chemical qualities of the waters", they nevertheless warn about "changes in quality which may be brought about by diluting the sample". Furthermore, Brown *et al* (1970) caution against over-liberal interpretation of laboratory studies; in fact, they state: "Unfortunately, results obtained

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from studies such as these have been taken previously as not only reasonably approximating, to a measure, the true acute lethal toxicity of the rivers investigated, but also as being adequate for the purpose of making predictions of the conditions necessary for fish to flourish in a river". In qualifying this statement, Brown *et al* (1970) noted that in most laboratory studies, besides the possible changes in toxicity due to handling of the samples, the fish used are usually well-fed vigorous adult fish, with no signs of disease or parasites, contrasting with the natural population where many of the fish may already be suffering "retrograde pathological changes caused by chronic poisoning or disease". In the same vein, Servizi *et al* (1966) have cautioned that conditions (i.e., oxygen, etc.) in a natural environment may be less favorable for fish than in laboratory conditions.

It would be very convenient if all pulp and paper operations discharged the same pollution load at the same rate, and into receiving waters that have comparable capacities, flow-rates, etc. It might then be possible to select a common dilution factor that would be directly applicable to all situations. But, unfortunately, such ideal intercomparable conditions do not exist, and any prospective dilution factor must consider the worst loading rate that may be encountered, especially as many receiving waters are already polluted. Some years ago, Gunter and McKee (1960) stated:

"Pollution control... falls short of its objective because it is normally tied to effluent requirements rather than to the quality of the receiving waters".

One rather obvious comment seems warranted: Effluent requirements have not always included consideration of such factors as *volume* of output (as a function of production-rate of a mill) or multi-purpose use of receiving waters. Lloyd (1972) has recently recommended that criteria should give *ranges* of concentrations, in considering the moderating influence of water factors such as pH, temperature, hardness, etc. prevailing in different receiving waters.

Perhaps the best way to end this presentation is with a comment by Walden (1965); although he was referring to kraft pulp mills, the viewpoint is applicable to all pulp and paper operations:

"The kraft pulp mill and fishing industries have cohabited on tidewater for many years with a reasonable degree of success. However, the minor difficulties that have arisen from time to time have indicated the need for increased fishery protection as the kraft pulp industry utilizes interior streams and lakes where less dilution is available... To maintain the economic position of both industries, sound technical knowledge is necessary to determine precisely the reaction of salmonid fish to kraft pulp mill effluents. This information must then be utilized to provide complete safety for our salmon runs. Anything more than this jeopardizes the economic position of our pulp industry. Anything less threatens the very existence of the fishing industry".

It is only necessary to add that the same consideration must be given to the many aquatic species and to the aquatic ecosystems themselves.

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SCIENTIFIC CRITERIA

The Scientific Criteria section of this report was prepared by members of the Advisory Panel. The pertinent sections in the foregoing document for each of the seven topics covered by the Panel are listed below:

TOPIC	SECTION IN TECHNICAL REPORT
1. pH	Appendix 5. INTRINSIC WATER FACTORS, section 3. The pH of the water. ADVERSE EFFECTS OF PULP MILL WASTES, sections d-ii) Sulfite, and d-iii) Kraft effluents. BIOASSAY, para. 2.
2. Dissolved Oxygen	Appendices 3 and 4. INTRINSIC WATER FACTORS, section 1. Dissolved Oxygen; and 2. The type of receiving water. ADVERSE EFFECTS OF PULP MILL WASTES, section d-ii) Sulfite, para. 5. BIOASSAY, para. 2.
3. Suspended Solids	Appendices 1 and 7. ADVERSE EFFECTS OF PULP MILL WASTES, section a) Suspended Solids. BIOASSAY, para. 3.
4. Color/Turbidity	ADVERSE EFFECTS OF PULP MILL WASTES, section a) Suspended Solids, para. 3.
5. Taste and Odor	ADVERSE EFFECTS OF PULP MILLS WASTES, section c) Toxicity of individual components, paras. 7 and 8.
6. Biochemical Oxygen Demand	Appendices 1, 8, 9 and 10. ADVERSE EFFECTS OF PULP MILL WASTES, sections b) Oxygen Demand, and d-ii) Sulfite, para 6.
7. Toxicity	Appendices 11, 12, 13, 14, 15 and 16. ADVERSE EFFECTS OF PULP MILL WASTES, all sections. BIOASSAY, total.

PULP AND PAPER WASTES

RECOMMENDATIONS OF THE ADVISORY PANEL

The overall effect of pulp and paper mill effluents on the aquatic environment may be subdivided into a number of individual effects, of which only seven are considered here. Although other effects are recognized, their relative importance and the information concerning them, at this point in time, do not merit their inclusion in this document.

1. pH

Acceptable pH limits for most receptors in receiving waters are known and are in the range 6.5 — 8.5, although exceptions do occur. Where natural background levels are outside this range, release of effluents within the range 6.5 — 8.0 normally is not considered detrimental, although the resultant pH of receiving waters may be below 6.5 or above 8.5. Situations where biological communities have been developed entirely outside this range are excepted. Permissible pH alteration will depend upon specific conditions, but abrupt changes of more than 0.2 pH units may be undesirable.

2. Dissolved Oxygen

For maximal protection of fish and other aquatic life, the minimum dissolved oxygen in any season should not be less than the estimated natural minimum concentration characteristic of that body of water for the same season. In estimating natural minima one may assume that surface waters are naturally saturated, unless there is scientifically valid evidence that they were lower in the absence of man-made changes. Deeper waters, except in vertically mixed situations, almost invariably undergo oxygen depletion during periods of prolonged high ambient atmospheric temperatures and should be monitored for at least a year to obtain the natural seasonal minimum.

For temperatures prevalent in most Canadian waters, release of effluents should not result in a diminution of Dissolved Oxygen in receiving waters below 9.0 mg/L. Where natural background levels are below this value, further depletion in oxygen levels is undesirable. The literature does not clearly support a concentration of 9.0 mg/L Dissolved Oxygen or a corresponding saturation value as a minimum requirement for protection of a given species, but it is presumed desirable for the protection of the aquatic ecosystem.

3. Suspended Solids

Data are not available which define absolutely a minimum acceptable concentration of suspended solids. Their impact on Dissolved Oxygen and color/turbidity should not result in a total impact exceeding values listed for these parameters. The concentrations of suspended solids which will form a fibre blanket on the bottoms of receiving waters are known to be highly dependent upon the settleability of the solids and the hydrodynamic characteristics of receiving waters. No value, acceptable to benthic receptors, can be put forward.

Suspended solids which are directly toxic to aquatic fauna, such as fish, require further definition of acceptable concentrations. Further differentiation of the effect of fibres from different wood species and various pulping processes is desirable. Present evidence suggests a lower limit of 25 mg/L may be acceptable for nekton-containing waters.

4. Color/Turbidity

Available data do not define the threshold levels of color/turbidity which detract from productivity of receiving waters. Aesthetically, any increase over the threshold level of visual perception which is 10 — 15 APHA units, is undesirable in waters of high clarity. Additional suggestions are that

the combined effect of both color and turbidity should permit at least 10% of the incident light to reach the bottom of any desired photosynthetic zone. Owing to the almost absolute paucity of information, further studies are required to produce useful numerical values.

5. Taste and Odor

Taste and odor problems in drinking water supplies and in fish flesh are associated with aromatic hydroxyl molecules derived during pulping. Limited data suggest 30 $\mu\text{g/L}$ aromatic hydroxyl molecules as an acceptable maximum concentration. Other compounds, i.e., the terpenes, "resin acids" and chlorinated lignin residues produced during bleaching, may be implicated. Data for defining criteria are not available. If chlorinated aromatics are involved, acceptable levels may be lower. Further studies are required.

6. Biochemical Oxygen Demand

The release of biodegradable carbonaceous materials should be such that criteria for dissolved oxygen are met. These materials, if they persist in receiving waters, may cause fungal slimes, e.g. *Sphaerotilus*. Although data substantiating maximum acceptable concentrations are scanty, the maximum concentration indicated to be satisfactory is 0.06 mg/L, as 5-day BOD (although this is below the range detectable with current methodology and represents a value obtained by experimental extrapolation). Further studies are required.

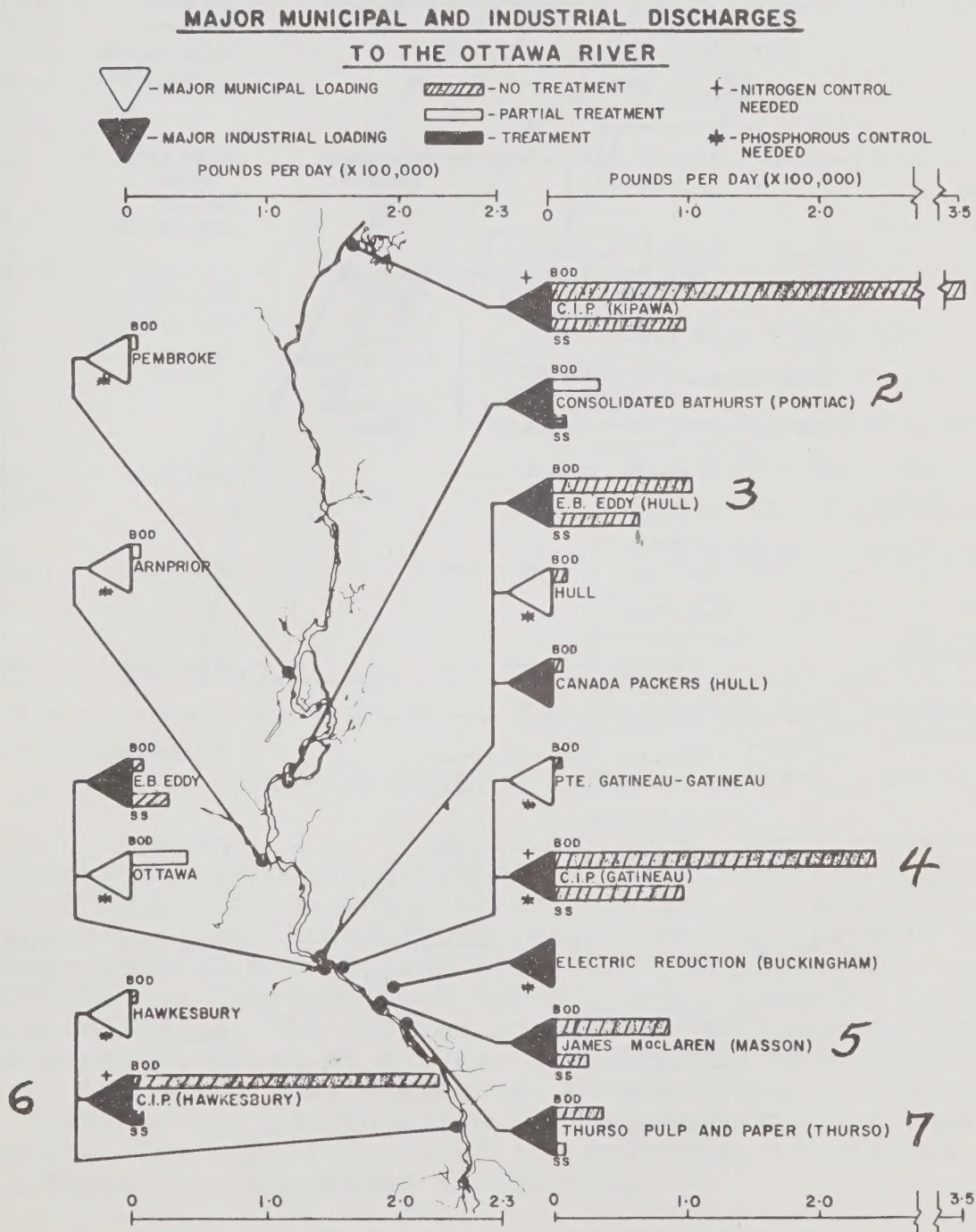
7. Toxicity

This important topic, on which very considerable data have already been amassed, still requires documentation of the short-term (acute) and chronic effects, as well as sublethal effects over the wide range of aquatic fauna at various stages of their life cycle. Furthermore, although many of the toxic moieties are known and their toxic role has been quantitatively assessed in some instances, the toxicity of pulp and paper effluents still is considered to be due to a poorly-defined complex mixture of organic molecules. Consequently, acceptable concentration of toxic substances cannot be defined absolutely and results usually are expressed in terms of LC_{50} data, which relate to short-term exposures. However, bioassay procedures which can indicate acceptable threshold levels, have been developed only for a limited number of aquatic species at specific stages in their life cycle. Thus, tentative criteria still require the use of "application factors" which relate toxicity to lethal 96-hr. LC_{50} concentrations, a procedure which has an extremely tenuous technical basis (unless the chosen "application factor" protects against the onset of sublethal stress). A better basis would relate to chronic exposure data, yielding "lethal or incipient lethal threshold" concentrations. Present data indicate that a probably acceptable value is 0.05 of the 96-hr. LC_{50} value for a representative, important and sensitive species of the aquatic fauna involved.

Considerable studies are still required before valid criteria for this important parameter are available. Ultimately, criteria will be based on the threshold level causing a sublethal effect in the most sensitive stage of the life cycle of a number of indicator aquatic species.

APPENDIX 1

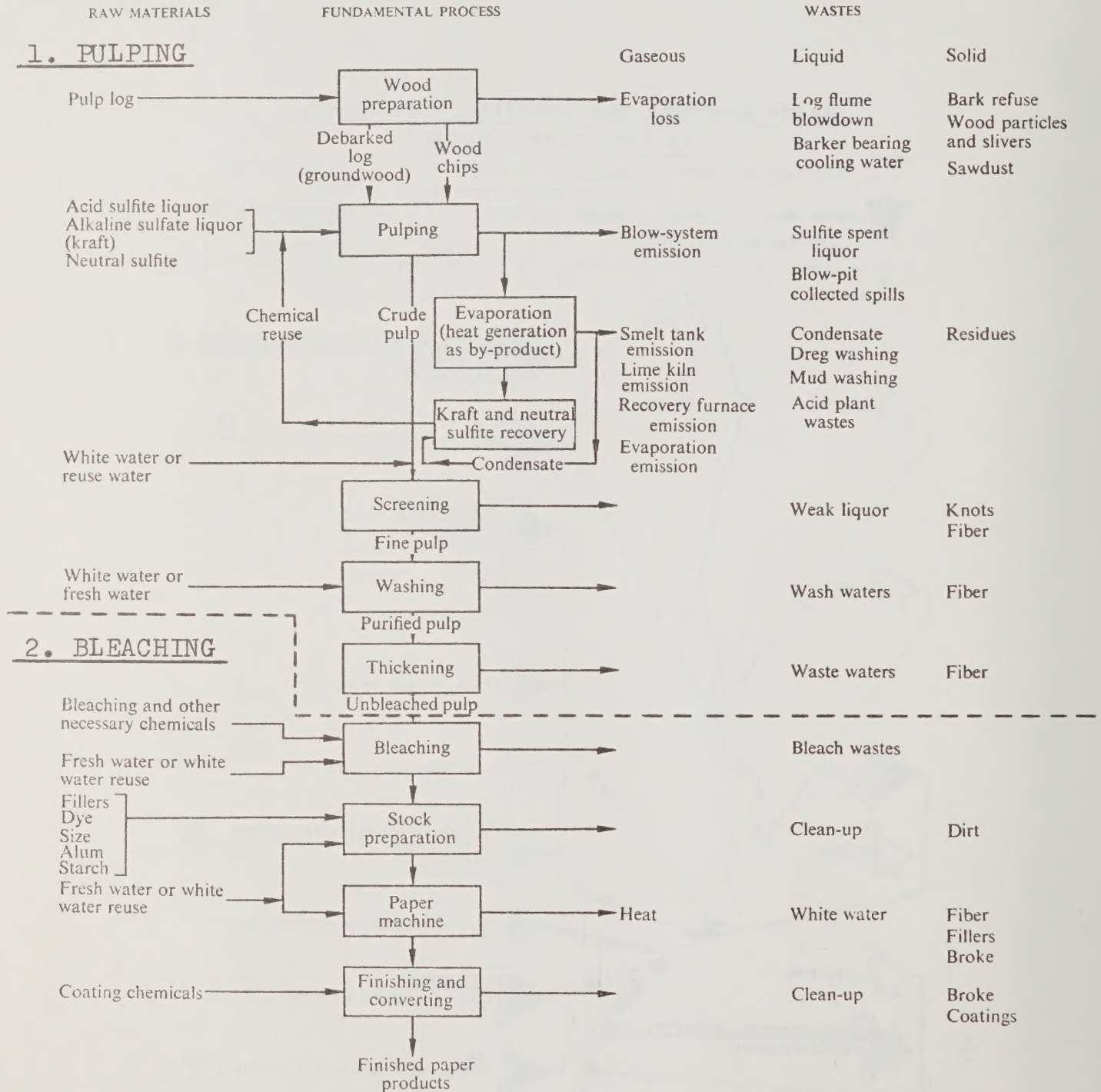
NOTE: This chart was prepared by the Ontario Water Resources Commission and the Quebec Water Board (O.W.R.C. and Q.W.B., 1971). Seven pulp mills are numbered on the chart in North-to-South order. The seven mills were discharging a total of 1,068,000 pounds of BOD plus 363,000 pounds of suspended solids per day. Depending on how you calculate it, the daily BOD load is equivalent to a city of 6 or 8 million people. A similar BOD loading has been reported in connection with pulp mills in the Maritimes (Row, 1972).



APPENDIX 2

(taken from Nemerow, 1971)

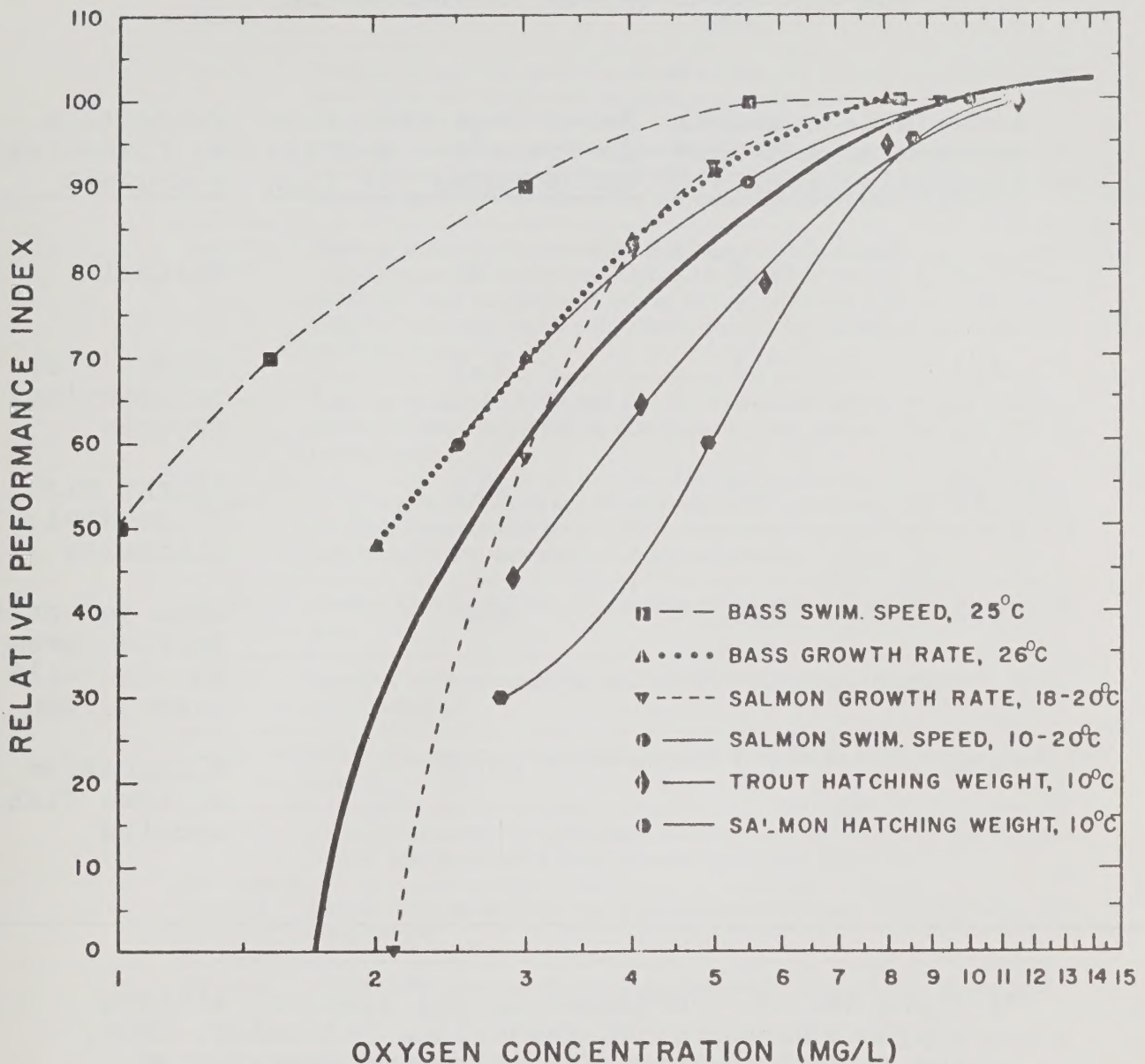
SIMPLIFIED FLOW-DIAGRAM OF PULP AND PAPER PROCESSES



APPENDIX 3

(taken from Doudoroff and Shumway, 1970)

FISH PERFORMANCES AT VARIOUS LEVELS OF DISSOLVED OXYGEN



"Impairment-of-performance responses" of freshwater fishes to reductions of oxygen concentration: Hypothetical "average" concentration-response curve (heavy line) generally agreeing with some plotted, representative relations between oxygen concentration and indices of relative "performance" (growth rate, swimming speed, or weight at hatching)... The plotted points are included mainly to facilitate identification of curves: they are all data reported somewhere in the text: some are actual observations, but most are estimates obtained by interpolation or by integration of experimental results. The significance of the ordinates ("relative performance indices") is explained in the text.

(Food and Agriculture Organization of the United Nations)

APPENDIX 4

ILLUSTRATION OF THE VARIOUS "LEVELS OF PROTECTION"

RECOMMENDED BY DOUDOROFF AND SHUMWAY (1970)

FOR DISSOLVED OXYGEN IN FRESHWATER

<u>Level of protection</u>	<u>Acceptable seasonal minimum oxygen concentration (mg/L)</u>		<u>Percentage reduction in "relative performance index" of fish</u>	<u>Protection to fisheries resources</u>
A	9.0*	7.5*	0	Maximal
B ₁	8.3	7.1	1.5	Slight risk to spawning grounds
B	7.7	6.8	3.0	Slight risk to general fisheries
C	6.2	5.6	9.0	Some reduction in fish production will occur often
D	4.4	4.1	20.0	Elimination of some fish species

*: These values correspond to the seasonal minimum oxygen concentration prevailing naturally. Thus, level-of-protection "A" allows no lowering in oxygen concentration.

NOTE: In the interest of brevity, the pattern is illustrated with only 2 concentrations of Dissolved Oxygen prevailing in a given body-of-water (i.e., 9.0 and 7.5 mg/L).

APPENDIX 5

(taken from EIFAC, 1969)

SUMMARY OF THE EFFECT OF pH VALUES ON FISH

Range	Effect
3.0-3.5	Unlikely that any fish can survive for more than a few hours in this range although some plants and invertebrates can be found at pH values lower than this.
3.5-4.0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4.0-4.5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only the last named may be able to breed.
4.5-5.0	Likely to be harmful to the eggs and fry of salmonids and, in the long term, persistence of these values will be detrimental to such fisheries. Can be harmful to common carp.
5.0-6.0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 ppm, or the water contains iron salts which are precipitated as ferric hydroxide, the toxicity of which is not known.
6.0-6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 ppm.
6.5-9.0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9.0-9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9.5-10.0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to development stages of some species.
10.0-10.5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10.5-11.0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11.0-11.5	Rapidly lethal to all species of fish.

Reference is made to different species on the basis of information known to us; the absence of a reference indicates only that insufficient data exist.

APPENDIX 6

SOME COMPONENTS OF PULP AND PAPER EFFLUENTS

<u>Wood preparation, groundwood, etc.*</u>	<u>Sulfite</u>	<u>Kraft</u>
Bark	Sulfur compounds (mostly sulfite)	Sulfur compounds (hydrogen sulfide; dimethyl sulfide; disodium sulfide; methyl mercaptan)
Knots	Sugars (arabinose, fructose, glucose, mannose, xylose)	Sugars (degradation products)
Pitch		
Sawdust		
Small fibers		
Resin acids	Lignin residues (sulfonate; chlorinated)	Lignin residues (thiolignin; chlorinated)
	Resin acids	Resin acids
	Acetone	Fatty acids
	Alcohols	Terpenes
	Furfural	Tetrachloro- o-benzoquinone
	Acids (formic; acetic)	
	Catechol	

*: These "wood preparation" contaminants are also present in the effluents produced by the Sulfite and Kraft processes.

Possible additives: chlorine, zinc, higher alcohols,
(mercurials?), pentachlorophenate, etc.

APPENDIX 7

(taken from EIFAC, 1964)

CRITERIA FOR LONG-TERM EFFECTS OF SUSPENDED SOLIDS

We present the following tentative criteria for discussion and comment.

With respect to chemically inert solids and to waters which are otherwise satisfactory for the maintenance of freshwater fisheries:

- (a) There is no evidence that concentrations of suspended solids less than 25 p.p.m. have any harmful effects on fisheries.
- (b) It should usually be possible to maintain good or moderate fisheries in waters which normally contain 25 to 80 p.p.m. suspended solids. Other factors being equal, however, the yield of fish from such waters might be somewhat lower than from those in category (a).
- (c) Waters normally containing from 80 to 400 p.p.m. suspended solids are unlikely to support good freshwater fisheries, although fisheries may sometimes be found at the lower concentrations within this range.
- (d) At the best, only poor fisheries are likely to be found in waters which normally contain more than 400 p.p.m. suspended solids.

In addition, although several thousand p.p.m. solids may not kill fish during several hours or days exposure, such temporary high concentrations should be prevented in rivers where good fisheries are to be maintained. The spawning grounds of salmon and trout require special consideration and should be kept as free as possible from finely divided solids.

These tentative criteria apply only to chemically inert solids and to waters which are otherwise satisfactory for the maintenance of freshwater fisheries.

(NOTE: In this EIFAC document, pulp and paper solids are only one of many types of suspended solids considered, as regards long-term effects on aquatic ecosystems.)

PULP MILL EFFLUENT CHARACTERISTICS re "LOADING RATE"

(assuming no external treatment of effluents)

per ton of product		BOD ₅ for a typical sampling-day		Reference source	
Waste, U.S. gallons	Total Soluble Solids, lb.	lb.	Population equivalent		
Sulfite (bleached)	50,470	2414	457*	2857	Nemerow (1971)
Kraft (bleached)	64,838	330	72*	451	Nemerow (1971)
Kraft (bleached)	49,500	560	79	494*	Paavila (1972)
Groundwood	2,302	7	3.2*	20	Nemerow (1971)

*: For intercomparison's sake, the calculation assumed that the average human accounts for sewage with a BOD of 0.16 lb./day.

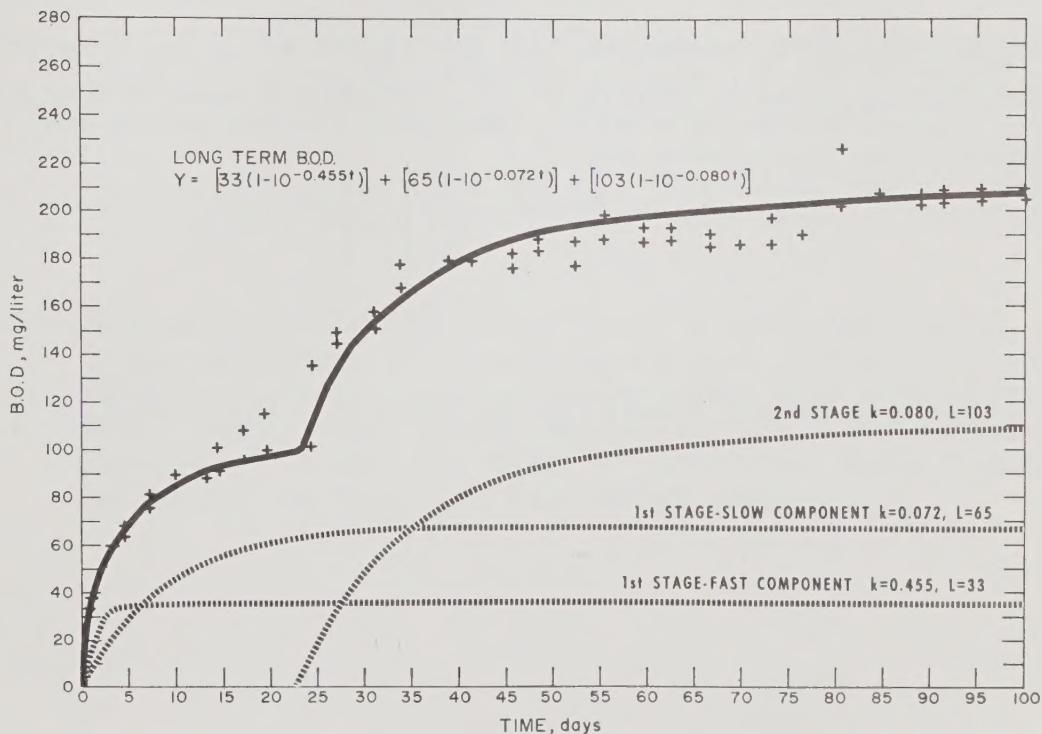
NOTE: It can be seen that the loading rate, i.e., "Waste, gallons" X "Total Soluble Solids, lb." is much greater for sulfite pulping (without chemical recovery) than for kraft processing, and -- in turn -- very much lower for groundwood pulping. Moreover, this trend is reflected in the 5-day BOD. Such considerations are important, especially in terms of what might be called "long-term attrition". For instance, if the loading rate exceeds (even slightly) the ability of the receiving waters to re-oxygenate, then the long-term prognosis -- especially in a lake or a non-tidal inlet -- portends a progressive degradation of the entire aquatic ecosystem.

APPENDIX 9

(taken from Raabe, 1968)

LONG-TERM BOD OF KRAFT MILL EFFLUENTS

NOTE: Raabe attributes the "1st stage fast" (one-sixth of the 100-day demand) to "oxidation of wood sugars and other readily decomposable materials". The other two stages, he terms "suggestive of the decomposition of the lignin and its by-products and other decomposable organics." It must be emphasized that this graph represents the BOD characteristics in receiving water downstream from a kraft pulp mill. In comparison, the 5-day BOD loading from a sulfite mill (i.e., one without a chemical recovery system) would be about 6 to 16 times greater.

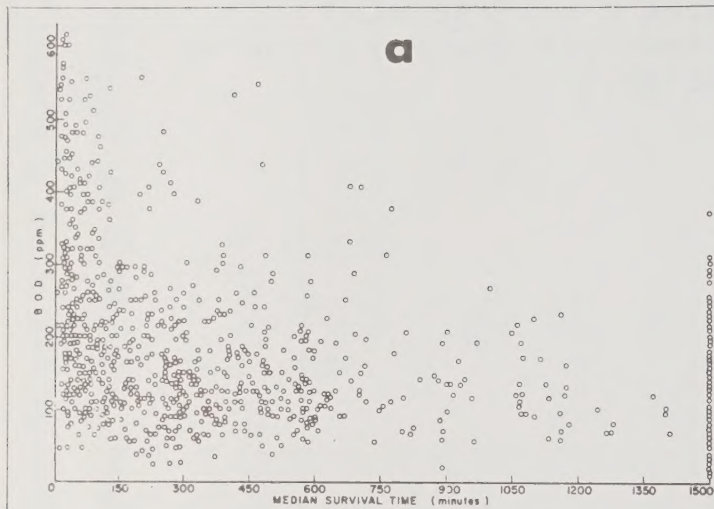


Long-term BOD over 100-day period.

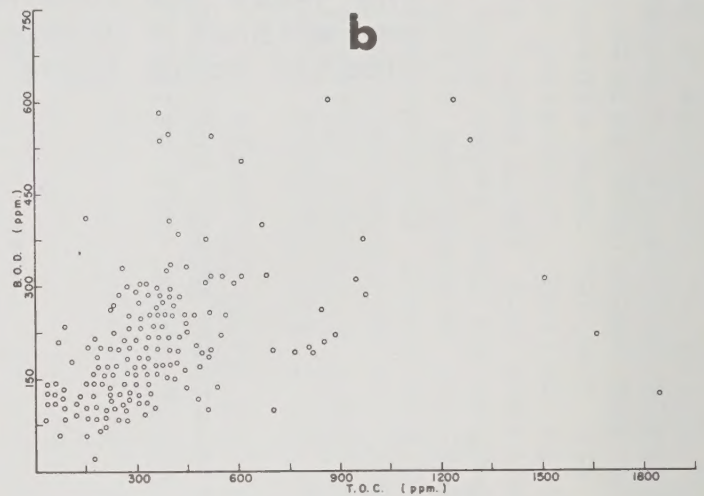
APPENDIX 10

(taken from Howard and Walden, 1971)

CORRELATIONS OF BOD WITH OTHER FACTORS



Combined plot of BOD₅ against toxicity (MST) for samples of unbleached white water, first chlorination effluent, first caustic extraction effluent, and total outfalls, from 7 bleached kraft pulp mills.



Plot of BOD₅ against TOC for combined outfall samples from 7 bleached kraft pulp mills.

(Pulp and Paper Magazine of Canada: Publishers)

APPENDIX 11

(taken from Haydu et al, 1952, and Van Horn et al, 1949)

TOXICITY-TO-FISH OF SOME SULFUR COMPOUNDS AND NaOH

Concentration (ppm) for 120-hr exposure			
	*	**	*
	<u>All fish survived</u>	<u>First fish died</u>	<u>All fish died</u>
Hydrogen sulfide	0.3-0.7	1.0	1.0-1.2
Methyl mercaptan	0.5-0.9	0.5	0.9-1.75
Disodium sulfide	1.0-1.8	3.0	3.0-3.5
Sodium hydroxide	10-27	100	20-48

*: Haydu et al: Range of values obtained with Chinook salmon, Coho salmon, and Cut-throat trout, at 12-15°C.

** : Van Horn et al: The same values were reported for minnows and Spotfin shiners, at 18°C.

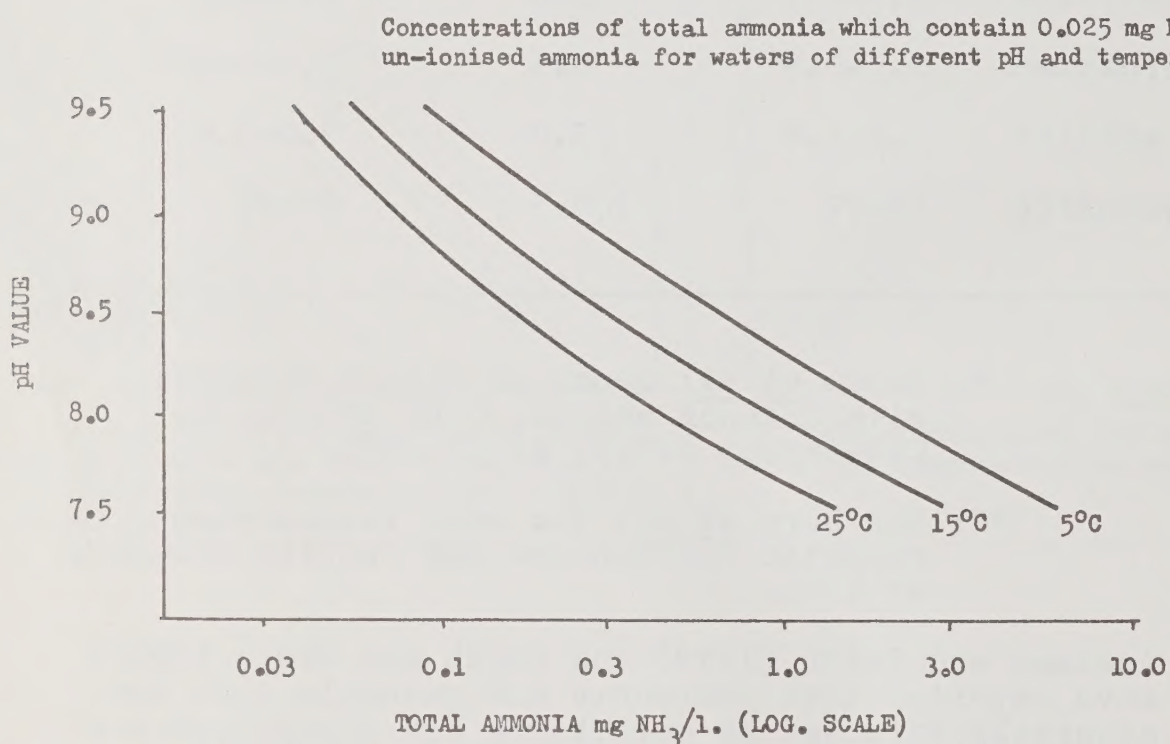
NOTE: Adelman and Smith (1970) and Smith and Oseid (1970) have reported that embryonic and juvenile fish are adversely affected by waterborne H₂S concentrations much lower than those shown in the above Table. However, it may be well to consider such findings as being in the "preliminary" stages.

APPENDIX 12

(taken from EIFAC, 1970)

VARIATION OF AMMONIA CONCENTRATION WITH pH AND TEMPERATURE OF WATER

Although concentrations of un-ionized ammonia below 0.2 mg NH_3/L may not kill a significant proportion of a fish population, they may still exert an adverse physiological or histopathological effect... On balance, therefore, a concentration of 0.025 mg NH_3/L (12% of the threshold LC_{50} of 0.2 mg NH_3/L unionized ammonia) may be the maximum which can be tolerated by fish for a long period.



APPENDIX 13

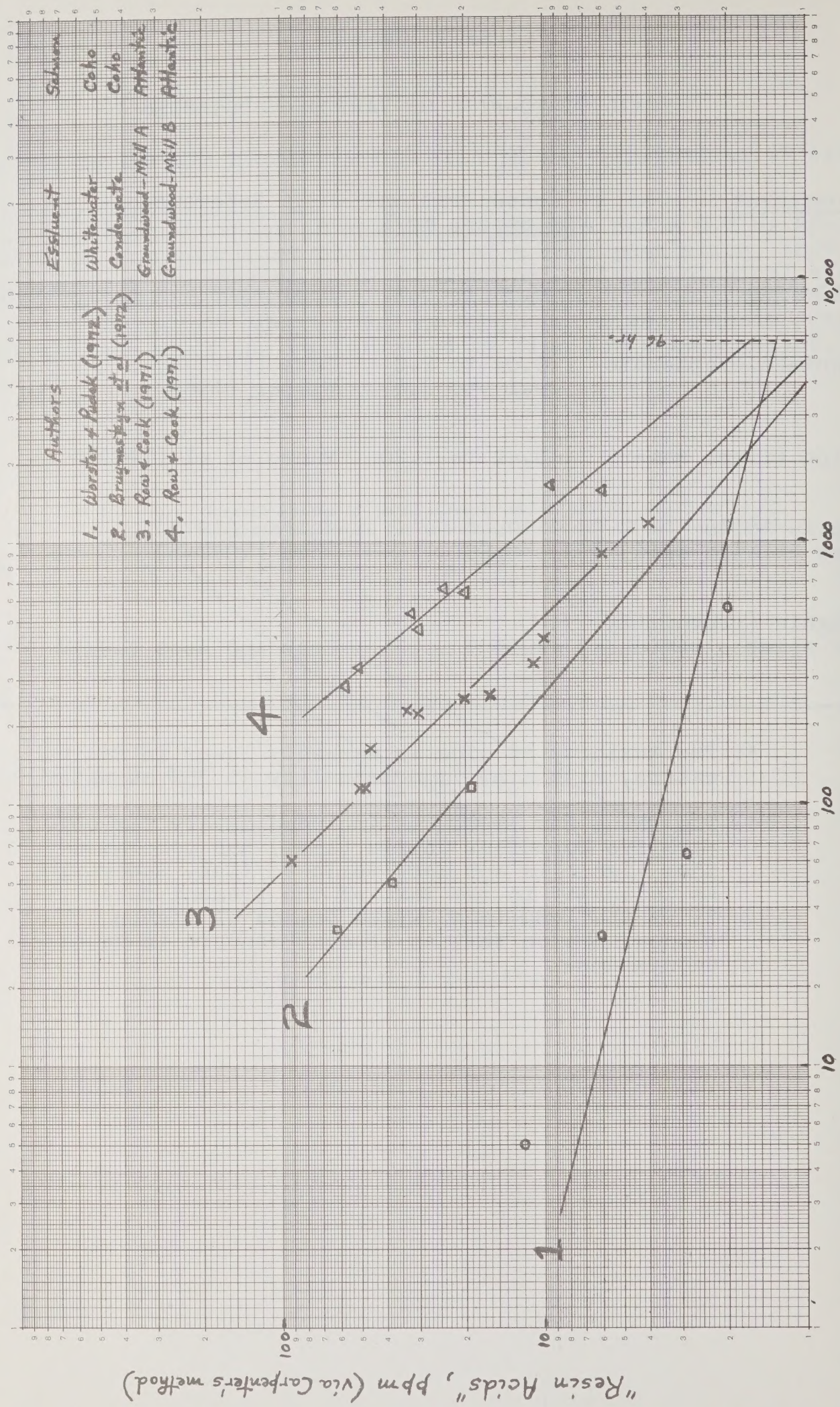
TOXICITY-TO-FISH OF VARIOUS SUBSTANCES

<u>Component</u>	<u>Concentration in water, mg/L</u>	<u>References</u>
Chlorine	0.05 to 0.2	Doudoroff and Katz (1950)
Pentachlorophenate	0.04 to 2.0 0.2 to 0.6	Côté (1972-a) Wilber (1969)
Zinc (fresh water)	0.42 to 1.20	Munro <u>et al</u> (1972)*
Resin Acids) (as Abietic acid))	0.44 0.65	Walden (1972) Côté (1972-b)
Lignin (presumably as soluble residues)	1000**	Cook and Hoos (1971)

*: The toxicity of zinc is markedly lower in saline waters, with a minimum lethality at 35% seawater.

** : The value for lignin is included merely for comparative purposes. Chopin (1959) has concluded that lignin is not very toxic to fish. However, as indicated in the text of the present report, it is the long-term Oxygen Demand of lignin biodegradation that is of most concern in aquatic ecosystems.

APPENDIX 14: TOXICITY OF "RESIN ACIDS"



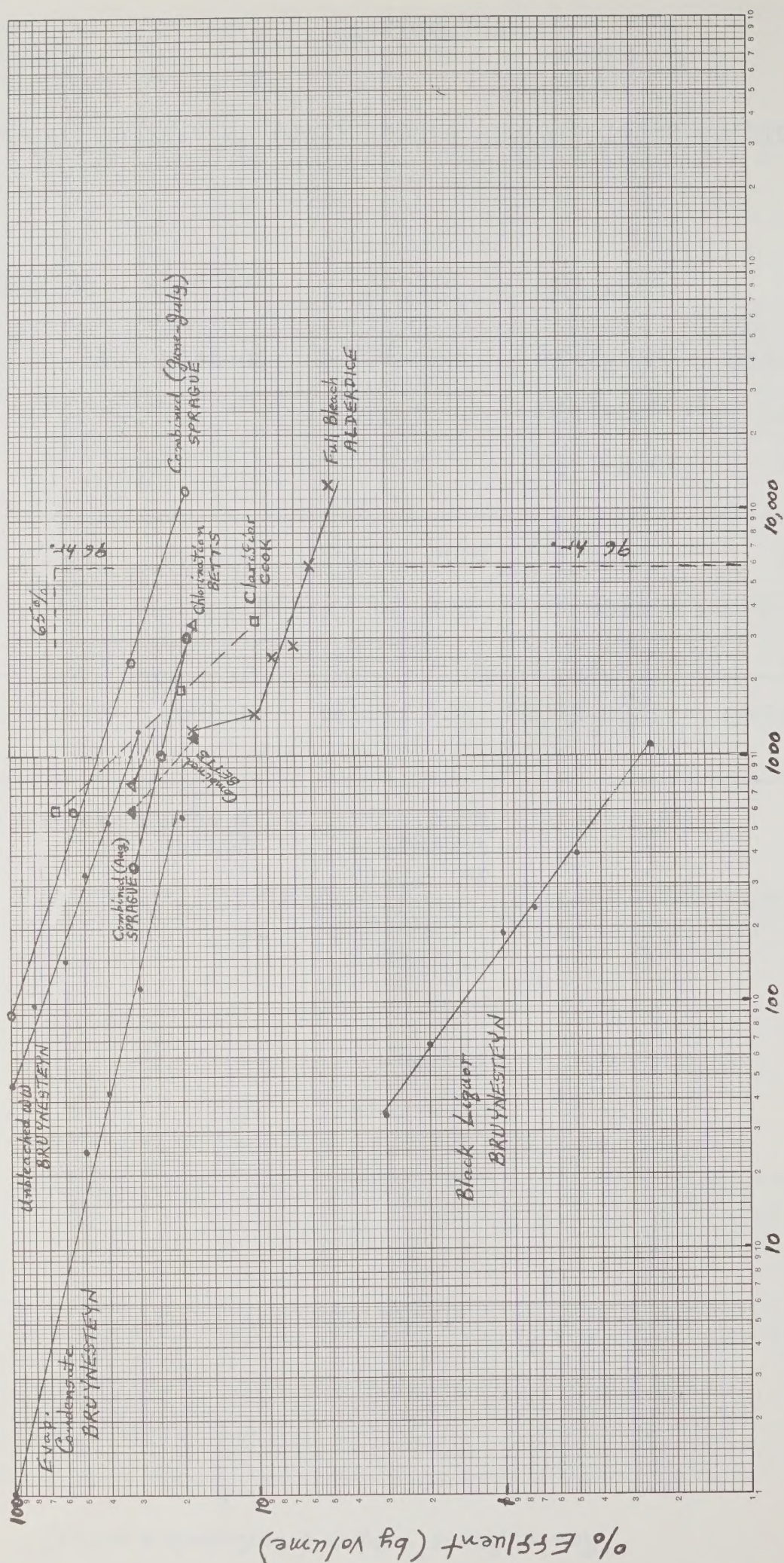
Time (minutes) to kill 50% of the fish

APPENDIX 15

TOXIC EFFECTS OF SULFITE WASTE LIQUOR (SWL) ON VARIOUS AQUATIC SPECIES

Species	SWL, ppm	Effect	Exposure	Authors
Chinook salmon	560-1175	5% killed	30 days	Williams <u>et al</u> (1953)
Pink salmon	530-1530	"	"	"
Coho salmon	1015-1230	"	"	"
Brown trout	500	100% killed	9 days	Grande (1964)
"	100	25% "	22 "	"
Atlantic salmon	2000-2400	50% killed	4 days	Wilson (1972)
Oysters	2.5	Food organisms depressed	Several months	Woelke (1960)
		<u>Reproductive cycle</u>		
"	2	Abortion, etc.	"	"
"	8	Abnormal	"	"
"	16	Interrupted	"	"

APPENDIX 16: TOXICITIES OF VARIOUS KRAFT MILL EFFLUENTS REPORTED BY DIFFERENT AUTHORS



Time (minutes) to kill 50% of the fish

APPENDIX 17

LIST OF TOPICS COVERED IN SPRAGUE'S REVIEWS

I: 1969 -- Methodology for the test:

Static bioassay, with the solution changed daily.
Continuous-flow bioassay, using minimum flow-rate.
Equipment and instrumentation.
The use of a group of similar fish, usually 10.
Acclimation of the fish (2 weeks for temperature changes).
Randomization in fish selection.
Terminology, measurement, and recording.
Toxicity curves and thresholds.
Degrees of toxicity.
Duration of bioassay (at least 4 days).
Mortality in control fish.
Estimating error.

II: 1970 -- Interpretation of acute toxicity:

Antagonism, synergism, or potentiation.
Modifying factors (water hardness, temperature, oxygen, pH).
Multivariant analysis (fluctuating concentrations).
Acclimation of fish.
Comparison of fish species.
Organisms other than fish.
Autopsy methods.

III: 1971 -- Sublethal response:

Growth
Performance
Respiration
Disease resistance
Behavior
Reproduction

Field studies:

Bioassays
Ecological surveys
"Safe" concentrations
Application factors

NOTE: The author of the present report has received comments about the above tabulation, i.e.,
(a) the non-inclusion of a section on Aeration;
(b) the questionable relevance of Autopsy methods to evaluate toxic effects of pulp and paper effluents.

APPENDIX 18: PART I

TYPE OF MILL PROCESS	PROCESS EFFLUENT STREAMS AND OTHER DISCHARGED	EFFLUENT DILUTION AND OTHER FACTORS	TOXICITY FOUND	CRITERIA FOR TOXICITY EVALUATION	BIOASSAY TEST PROCEDURE								AUTHOR REFERENCE			
					Type of Bioassay		SPECIES	# of Fish per test	Feeding	D.O.	pH	Temperature		Filtration	Sample Storage	Other Test Information
					Replacement Frequency	Duration of Test										
Kraft	Primary Treatment Waste: Clarifier 10 (Table 2)	65% 20 3528 5 2 1	610 min. 1848 3528 > 5760 > 5760	TLM minutes re 50%	Static	96 hr.	Juvenile Atlantic Salmon	10	76 ppm.	No adjustment	approx. 4°C (Table 5)	No			Cook and Hoos 1971	
	Debarker (Table 1)	65%	Low=12 min. High (5 samples) =>5760 Av. of other 59 samples =approx. 8 hr. (480 min.)													
Kraft	Unbleached White Water	Hemlock TOC=655 mg/l 324 164 Softwood mix TOC=303 152 76 Pine TOC=324 162 81	>4 min. 252 445 64 min. 237 > 5760 <5 min. 65 140	MST minutes re 50%			100 day old Coho Salmon	11	S'n N'dl 2C	No adjustment		Yes	> 5 days		Worster and Pudek 1972 (Tables 4,5, and 6)	

APPENDIX 18: PART ii PULP AND PAPER MILL TOXICITY INFORMATION - LITERATURE REVIEW CHART

TYPE OF MILL PROCESS	PROCESS EFFLUENT STREAMS DISCHARGED	EFFLUENT DILUTION AND OTHER FACTORS	TOXICITY FOUND	CRITERIA FOR LETHAL TOXICITY EVALUATION	BIOASSAY TEST PROCEDURE			SPECIES	# of fish per test	Feeding	D.O.	pH	Temperature	Filtration	Sample Storage	Other Test Information	AUTHOR REFERENCE
					Type of Bioassay	Replacement Frequency	Duration of Test										
Sodium Sulfite	Unbleached White Water	Hemlock TOC=1288 mg/l 965 644 324 Softwood mix TOC=648 481 392 324 Pine TOC=324 162 81	14 min. 78 249 >5760 94 97 134 562 31 76 230	MST minutes re 50%				100 day old Coho Salmon	11								Worster and Pudek 1972 (con't)
Sulfite + Oxygen	Unbleached White Water	Hemlock TOC=1296 648 324 Softwood mix TOC=1007 353 Pine TOC=732 324	904 >5760 >5760 5760 5760 1509 >5760														

NOTE: A TOC of 324 mg/l was the average COD of B.C. effluents (Howard, 1971)
(for unbleached white water)

APPENDIX 18: PART iii

TYPE OF MILL PROCESS	PROCESS EFFLUENT STREAMS DISCHARGED	EFFLUENT DILUTION AND OTHER FACTORS	TOXICITY FOUND	CRITERIA FOR LETHAL TOXICITY EVALUATION	BIOASSAY TEST PROCEDURE					AUTHOR REFERENCE						
					Type of Bioassay		SPECIES	# of Fish per test	Feeding	D.O.	PH	Temperature	Filtration	Sample Storage	Other Test Information	
					Replacement Frequency	Duration of Test										
Kraft Pulp (coniferous wood)	Blend 40% Chlorination 30% Caustic 30% Screen-room (See orig'l report for more details)	June-July 100% strength 56% 32% 19% 10%	June-July 90 min. 600 2400 12000 > 18000	MST minutes re 50%	Twice per week	2 to 3 weeks	Juvenile Atlantic Salmon parr	5	once per day	Bubbler	7	15°C No?			Sprague and McLeese 1968-a (See Fig. 1)	
		August 32% strength 24% 19% 10%	360 min. 1000 3000 > 12000													
	Neutralized Bleached Effluent	100% Effluent Fresh 1 week holding 2 week holding 1 week B.O. 2 week B.O.	150 min. 3960 10080 > 10080 > 10080	MST minutes re 50%											Sprague and McLeese 1968-b (See "Results")	

APPENDIX 18: PART V

TYPE OF MILL PROCESS	PROCESS EFFLUENT STREAMS DISCHARGED	EFFLUENT DILUTION AND OTHER FACTORS	TOXICITY FOUND	CRITERIA FOR LETHAL TOXICITY EVALUATION	BIOASSAY TEST PROCEDURE			PROCEDURE							AUTHOR REFERENCE		
					Type of Bioassay	Replacement Frequency	Duration of Test	SPECIES	# of Fish per test	Feeding	D.O.	PH	Temperature	Filtration		Sample Storage	Other Test Information
Kraft	Un-neutralized		Effluent % by Volume	TLM conc'n req'd to kill 50% in 96 hr.	Daily	96 hr.	Common Guppy	10	No	> 4.0 ppm.	7.0 to 7.4	23 ± 1.5°C	Yes	No		Howard and Walden 1965 (Table 2)	
	Whole Effluent (pH 3.3)		8.4 to 10.1														
	Neutralized																
	Bleach plant acid sewer		18.2 to 35.4														
	Bleach plant caustic sewer		22.1 to 51.3														
	Brown stock screening + deckering		50.0 to 53.0														
	Whole Effluent		48.3 to 56.0														
	Un-neutralized Whole Effluent		12.2		Daily	96 hr.	Sockeye Salmon under-yearlings	10		Continuous Aeration	15 ± 1°C					(Table 3)	
	Neutralized Whole Effluent		34.2 to 64.1														
	Neutralized Bleach Effluent	0 Storage 2d. Storage	37.1% 41.0			96 hr.	Sockeye Salmon Under-yearlings									(Table 5)	
		0 Storage 5d. Storage	29.1 46.0														

PULP AND PAPER MILL TOXICITY INFORMATION - LITERATURE REVIEW CHART

[illegible]

PULP AND PAPER MILL TOXICITY INFORMATION - LITERATURE REVIEW CHART

[illegible]

APPENDIX 19

(summarized from the data of McLeay, 1972)

CHANGES IN BLOOD PARAMETERS OF COHO SALMON ON EXPOSURE TO KRAFT EFFLUENT

Coho salmon: Blood parameter	Degree of exposure to neutralized Kraft whitewater	
	<u>"acute 12-hour"</u>	<u>"chronic 25-day"</u>
Immature red blood cells	Signif. increased	Signif. increased
Hematocrit	Unchanged	Decreased
Thrombocytes	Much lower	Unchanged
% small lymphocytes	Unchanged	Decreased
% neutrophils	Unchanged	Greatly increased
Number of small lymphocytes	Markedly decreased	Unchanged
Neutrophil count	Unchanged	Elevated
Plasma glucose	Increased	Decreased

(Note the different response to the two types of exposure,
especially in such components as plasma glucose)

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THE EFFECTS OF PULP AND PAPER WASTES, WITH PA
ATTENTION TO FISH AND BIOASSAY PROCEDURES FOR

**RESOURCE CENTRE
INST. FOR ENVIRON'L. STUDIES
UNIVERSITY OF TORONTO**



